



Kinetic study of epoxidations by urea–hydrogen peroxide catalyzed by methyltrioxorhenium(VII) on niobia

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Abstract

Relative rates were measured for the heterogeneous epoxidation of olefins with urea–hydrogen peroxide (UHP) in CDCl_3 catalyzed by MeReO_3 on Nb_2O_5 . The rates are more selective than those in homogeneous MTO– H_2O_2 solutions. The reactivity orders among the alkenes are *cis* > *trans* and electron-rich > electron-poor. A molecular structure has been proposed for the active rhenium species which allows the rate differences to be explained in terms of energy gap between the alkene occupied $\pi(\text{C}-\text{C})$ and unoccupied $\sigma^*(\text{O}-\text{O})$ of the peroxorhenium moiety. © 2003 Elsevier B.V. All rights reserved.

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1. Introduction

Methyltrioxorhenium(VII) (CH_3ReO_3 , abbreviated as MTO), following the Herrmann group's discovery of its remarkable catalytic properties [1], has emerged as a useful catalyst for a number of organic transformations, especially epoxidations [2–5]. Owing to undesirable epoxide-opening and rearrangement reactions in ligand-free MTO-catalyzed epoxidations, attention has been given to the development of alternative procedures [6–10]. Sharpless and co-workers [7] discovered that addition of pyridines within a certain window of concentration [11] protected the epoxide products and enhanced catalyst activity.

There has been growing interest in the study of niobium-based materials as catalysts in various catalytic transformations [12–15]. Niobium(V) oxide can be used as a support, as a promoter, and also as a unique solid acid. Bouh and Espenson [10] have reported that there are several advantages of this heterogeneous catalyst for epoxidations, including easy workup and isolation of products, the avoidance of ring-opened products, and the recoverability and reuse of the catalyst.

Despite the importance of MTO– Nb_2O_5 in organic chemistry [10,16–18], kinetic studies have not been reported.

The present study was designed to evaluate the kinetics of epoxidation reactions with the insoluble compound urea–hydrogen peroxide (UHP). Vegetable oils and fats are important renewable raw materials for the chemical industry and their epoxidations provide versatile intermediates for industrial applications [19]. Thus, the rates of epoxidation of unsaturated fatty acids and esters were also determined.

The rates measurements referred do not, of course, give rise to absolute rate constants. Data for a single olefin would be nearly meaningless, because from one substrate to the next the control of key reaction variables would be impossible. Even something as simple as the rate of stirring could affect the rate. Consequently, dual substrates were used in every experiment; by the equations presented a rate constant ratio could be determined. This procedure, repeated for other pairs of substrates, allowing the relative rate constants for the entire series to be evaluated.

2. Experimental

2.1. Materials

CH_3ReO_3 (MTO) was prepared according to the literature procedure [20]. A standard pretreatment procedure of MTO– Nb_2O_5 has been described in the literature [10,21]. The olefins and UHP were purchased from Aldrich and used as received.

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2.2. Kinetic measurements

Concurrent reactions of two alkenes with UHP and MTO–Nb₂O₅ were conducted, aliquots being removed periodically. The concentrations of each the alkenes was calculated by integrating the ¹H NMR resonances of the alkenes and epoxides. The two substrates for a given experiment were chosen so as to give well separated resonances for the alkenes and epoxides. The general experimental procedure is described for the pair 2-pentene and cyclohexene. A small vial was charged with MTO–Nb₂O₅ (337 mg, 23 μmol Re) in CDCl₃ (3.5 ml), 2-pentene (0.100 ml, 0.927 mmol), cyclohexene (0.100 ml, 0.987 mmol), and then with UHP (132 mg, 1.4 mmol). The mixture was stirred at room temperature. Aliquots were withdrawn at intervals suitable for the reaction time, and then analyzed by ¹H NMR spectroscopy (Varian VXR300). Typically 11 samples were taken during an experiment.

3. Results

A mixture of substrates A₁ and A₂, each of which reacts separately with B in the presence of catalyst C, gives rise to two reactions that lead to independent products



The assumption can be made, and subsequently verified, that each reaction rate is first-order with respect to alkene concentration. The form of the dependences on UHP and MTO–Nb₂O₅ are not specified, except that the claim is made that the functional form, designated as *F* will be the same for both alkenes. Thus, the rate law for each reaction takes the form

$$-\frac{d[A_1]}{dt} = k_1[A_1]F \quad (3)$$

$$-\frac{d[A_2]}{dt} = k_2[A_2]F \quad (4)$$

The quotient of the rates is thus independent of factor *F*:

$$\frac{d[A_1]/dt}{d[A_2]/dt} = \frac{k_1[A_1]}{k_2[A_2]} \quad (5)$$

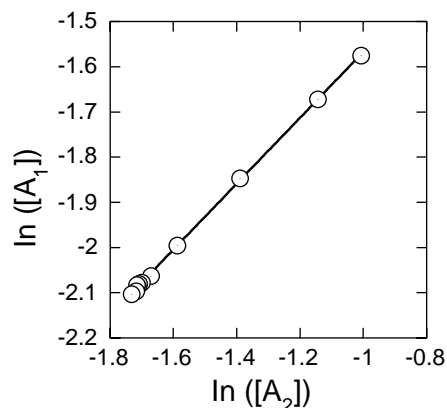


Fig. 1. Plot of $\ln[A_1]_t$ vs. $\ln[A_2]_t$ during the competitive epoxidations of 2-methyl-1-pentene (A₁) and cyclohexene (A₂) by MTO/Nb₂O₅–UHP at room temperature. The relative rate is given by the slope of this double-logarithmic plot. Reaction conditions: $[A_1]_0 = 0.23 \text{ mol l}^{-1}$, $[A_2]_0 = 0.42 \text{ mol l}^{-1}$; the amounts of UHP and Re are 1.4 mmol and 23 μmol, respectively, in 3.5 ml CDCl₃.

Integration yields an equation

$$\ln[A_1]_t = \frac{k_1}{k_2} \ln[A_2]_t - \frac{k_1}{k_2} \ln[A_2]_0 + \ln[A_1]_0 \quad (6)$$

According to this result a plot of $\ln[A_1]_t$ versus $\ln[A_2]_t$ should define a straight line with a slope k_1/k_2 .

To test the method, data for the pair of substrates 2-methyl-1-pentene and cyclohexene is presented in a double logarithmic plot in Fig. 1. Table 1 lists the relative rate constants under the different reaction conditions. When the concentration ratio is varied from 1:6 to 8:1, the values of k_1/k_2 change by 8.2%; likewise they differ by 13% with the amount of Re and 8% with UHP. These small changes show the acceptable precision of the method used; of course, the precision of the fit within one experiment exceeds the realistic precision of the entire set of determinations taken together.

A second method can be used to further prove the above method. If k_a/k_b and k_b/k_c or k_c/k_b are known, k_a/k_c can be obtained by a simple calculation,

$$\frac{k_a}{k_b} \times \frac{k_b}{k_c} = \frac{k_a}{k_c} \quad (7)$$

For example, the relative rate constants of each pairs among 2-methyl-1-pentene (a), 1-hexene (b) and cyclohex-

Table 1
Relative rates of epoxidations under different reaction conditions^{a, b}

Re = 23 μmol, UHP = 1.4 mmol		Re = 23 μmol, A ₁ :A ₂ = 1:2		A ₁ :A ₂ = 1:2, UHP = 1.4 mmol	
A ₁ :A ₂	<i>k</i> ₁ / <i>k</i> ₂	UHP (mmol)	<i>k</i> ₁ / <i>k</i> ₂	Re (μmol)	<i>k</i> ₁ / <i>k</i> ₂
1:6	0.674(3)	0.85	0.738(9)	10	0.674(4)
1:2	0.729(5)	1.4	0.729(5)	23	0.729(5)
8:1	0.699(9)	2.8	0.65(1)	41	0.713(8)

^a A₁, 2-methyl-1-pentene; A₂, cyclohexene; catalyst, MTO–Nb₂O₅; oxidant, UHP, in CDCl₃ at ca. 23 °C.

^b The number in parentheses is 1S.D. of the fit.

Table 2
Relative rates of epoxidation of various olefins with MTO/Nb₂O₅-UHP^{a, b}

Olefin	k_i/k_{ref}
2,3-Dimethyl-2-butene	127(1)
1-Methylcyclohexene	16.1(10)
2-Methyl-2-pentene	14.3(7)
<i>cis</i> -Cyclooctene	2.23(2)
<i>cis</i> -2-Pentene	1.02(1)
Cyclohexene	1 (ref)
<i>cis</i> -2-Hexene	0.904(2)
2-Methyl-1-pentene	0.70(2)
2,3-Dimethyl-1-butene	0.568(3)
<i>trans</i> -2-Hexene	0.409(7)
1-Hexene	0.0380(4)
1-Octene	0.0359(8)
3,3-Dimethyl-1-butene	0.0239(4)

^a In CDCl₃ at ca. 23 °C.

^b The number in parentheses is 1S.D. of the fit.

ene (c) were measured, giving $k_a/k_c = 0.70(2)$, $k_b/k_c = 0.0380(4)$, so $k_a/k_b = 18.4(3)$, as compared with the experimental value $k_a/k_b = 15.8(4)$.

Table 2 gives the rate constants relative to cyclohexene. The values increase regularly with the number of (electron-donating) alkyl substituents on double bond, from mono- to tetra-substituted compounds. A plot of k_i/k_{ref} versus the substituent number (N) is shown in Fig. 2, illustrating an apparent linear relation that spans over three orders of magnitude in reactivity, reflecting that the more electron-rich an olefin, the faster it is epoxidized.

Steric factors have a mild effect on the rates. In a series of mono-substituted olefins, the *tert*-butyl group in 3,3-dimethyl-1-butene is much more bulky than *n*-butyl group in 1-hexene and *n*-hexyl group in 1-octene, but their relative rates are very comparable,

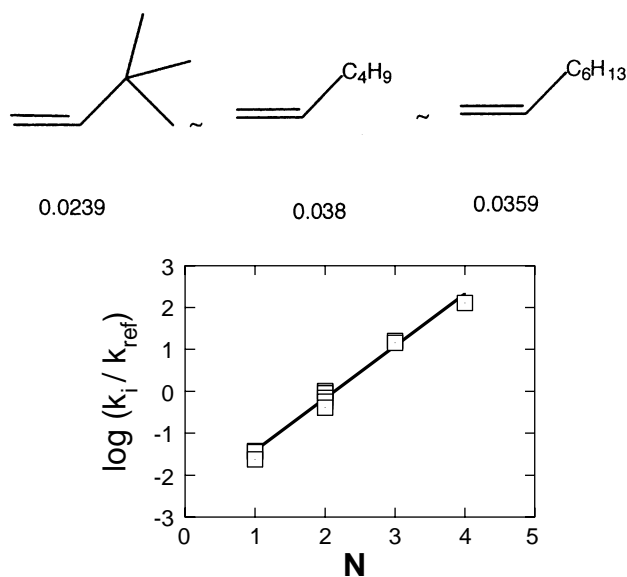
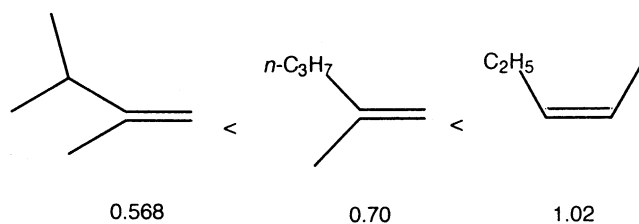
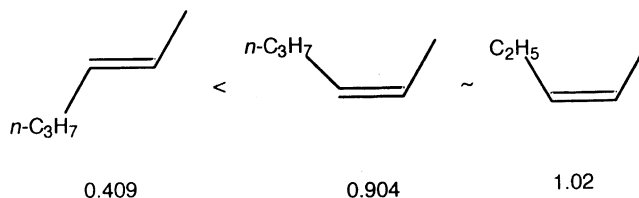


Fig. 2. Correlation of the relative rate constants, k_i/k_{ref} , with the substituents (N) on the double bond.

The same holds true in di-substituted olefins, such as these,



However, the relative rates of *cis*- and *trans*-olefins are significant different,

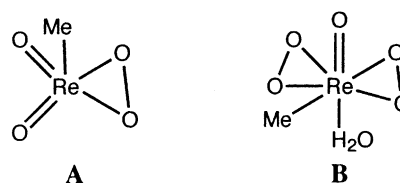


Overall, the above results clearly show that there are very similar epoxidation behaviors [18] in the heterogeneous and homogeneous catalytic systems (MTO/Nb₂O₅-UHP versus MTO-H₂O₂ in solution), namely, electronic factors are dominant, whereas the rates are relatively insensitive to steric factors.

The rates of unsaturated fatty acids and esters were measured relative to that of cyclohexene, as shown in Table 3. There are several features to note. First, the rates are not influenced by the change of the molecule from acids to esters; second, the rate of the *cis*-olefin is faster than its *trans* counterpart; third, the rates become slower with the increase of the number of double bonds in the olefins.

4. Discussion

The data clearly establish that electron-rich groups on the olefin increase the reaction rate. The reaction is insensitive to steric effects but *cis* > *trans*. The epoxidation mechanism with homogeneous MTO-H₂O₂ has been extensively studied experimentally [22,23] and computationally [24–27]. It has been shown that peroxorhenium species **A** or **B** are the catalytically active intermediates. The peroxide group, so activated, is attacked by the olefin via a spiro-structure to form the epoxide.



It is instructive to compare the heterogeneous and homogeneous rate constants (Table 4), which are expressed relative to that of cyclohexene. Epoxidation shows more selectivity with MTO/Nb₂O₅-UHP than with MTO-H₂O₂. For instance, in MTO/Nb₂O₅-UHP, the epoxidation rate of

Table 3

Rates of various fatty acids and esters relative to that of cyclohexene in MTO/Nb₂O₅-UHP^{a,b}

Unsaturated fatty acid and ester	k_i/k_{ref}
	0.97(2)
X = COOH, oleic acid X = COOCH ₃ , methyl oleate	1.04(1)
	0.35(2)
X = COOH, elaidic acid	
	0.76(2)
X = COOH, linoleic acid X = COOCH ₃ , methyl linolenate	0.71(2)
	0.51(1)
X = COOH, linolenic acid X = COOCH ₃ , methyl linolenate	0.51(1)

^a In CDCl₃ at ca. 23 °C.^b The number in parentheses is 1S.D. of the fit.

Table 4

Comparison of rates in heterogeneous and homogeneous reactions relative to cyclohexene

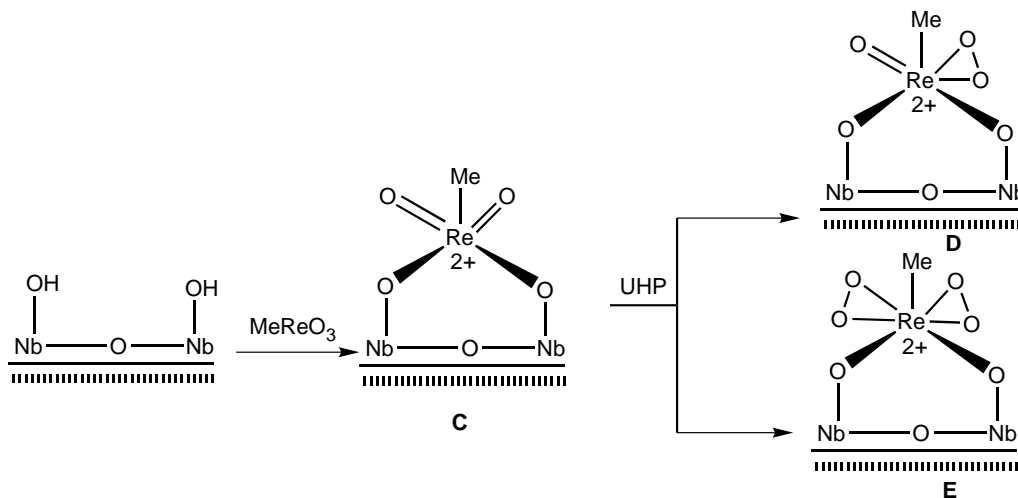
Olefin	k_i/k_{ref}^a	k_i/k_{ref}^b
2,3-Dimethyl-2-butene	128	12.3
1-Methylcyclohexene	16.1	3.0
2-Methyl-2-pentene	14.3	2.4
Cyclohexene	1	1
2-Methyl-1-pentene	0.70	56
1-Hexene	0.038	0.11
1-Octene	0.036	0.12
3,3-Dimethyl-1-butene	0.024	0.08

^a In CDCl₃ at ca. 23 °C for the MTO/Nb₂O₅-UHP system.^b From [18], in MeCN-H₂O for MTO-H₂O₂.

2,3-dimethyl-2-butene is 128 times faster than cyclohexene with UHP. Also, cyclohexene reacts 42 times faster than does 3,3-dimethyl-1-butene, whereas in MTO-H₂O₂, their corresponding values are both 12. An interesting question is

raised why the epoxidation reactivity exhibits these differences in different reaction media.

Supported MTO on niobia has been characterized previously by ¹³C MAS-NMR and FT-IR [17]. Surface acidity measurements showed that the surface of Nb₂O₅·*n*H₂O is strongly Brønsted acidic, even upon pretreatment at high temperatures [28–30]. Therefore, we propose that the surface contains Nb-OH groups that, as in the reaction MTO with 1,2-diols [31], can be condensed with two Re=O groups of MTO to form species C as illustrated in Scheme 1. Note that the weak conjugate base of a strong Brønsted acid behaves as a “weakly coordinating” anion [32–34]. Further evidence for this model comes from ¹³C NMR spectra. The weak coordination of anions leads to the rhenium center with more positive charge which is balanced by lessening of the electron density of the methyl group. Consequently, the methyl group resonance of MTO supported on niobia is down-shifted by 25 ppm with respect to that of MTO (in CDCl₃) at 19 ppm [35].



Scheme 1. Formation of heterogeneous peroxorhenium complexes.

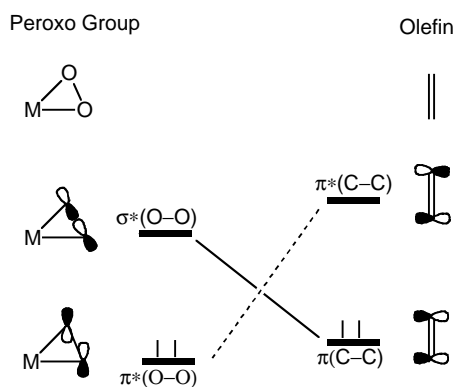


Fig. 3. Schematic representation of the frontier orbital interactions between a transition metal peroxo complex and an olefin.

Analogous to the homogeneous reaction between MTO and H_2O_2 [22,23], the species **C** reacts with UHP to form to the peroxorhenium compounds **D** or **E**. Owing to the weak coordination of peroxide anions, the rhenium center has less electron density compared to homogeneous **A** or **B**. This effect enhances the ability of supported MTO to withdraw electron density from the peroxo group. Therefore, the less negatively charged peroxo oxygen centers, **D** or **E**, are more amenable to nucleophilic attack by an olefin.

Recently, density functional calculations [25–27] on the reaction between a peroxo complex and an olefin showed that the dominating interaction occurs between the occupied (C–C) orbital of the olefin and the $\sigma^*(\text{O}–\text{O})$ LUMO of the peroxo group, while the other frontier orbital interaction between the occupied $\pi^*(\text{O}–\text{O})$ of the peroxo group and the unoccupied $\pi^*(\text{C}–\text{C})$ of the olefin is less important for the determination of the activation barrier (Fig. 3).

More electron-donating substituents on the double bond transfer electron density onto the C=C moiety and raise the $\pi(\text{C}–\text{C})$ energy. On the other hand, the more positive rhenium center is expected to decrease the $\sigma^*(\text{O}–\text{O})$ orbital level, resulting in a lower energy gap between the occupied orbital of the olefin and the peroxo LUMO, and more favorable epoxidation in the heterogeneous catalytic system.

trans-Alkenes are usually more stable than *cis*-alkenes, probably because of increased non-bonded repulsion in the *cis* isomer [36]; in other words, the $\pi(\text{C}–\text{C})$ energy of *cis*-alkenes is higher than that of *trans*-alkenes, and thus the energy gap between the occupied orbital of *cis*-alkenes and the peroxo LUMO decreases, favoring the epoxidation of *cis*-alkenes compared to *trans*-alkenes.

Theoretical studies [37,38] showed that increasing the degree of unsaturation of the vicinal bond increases the electronegativity. Linoleic and linolenic derivatives have one or two additional double bond(s) than oleic acid does, with one double bond bonded to two alkyl groups, so the electron density on the double bond decreases with inductive effect of the extra double bond(s), as a result, the rate order is oleic > linoleic > linolenic, which parallels the rates of epoxida-

tions with peroxyformic acid [39,40]. The calculated activation energies lie in the order ethylene > 1,3-butadiene > 2-methyl-1-propene.

In conclusion, the relative rates measured for UHP epoxidation in CDCl_3 in the presence of $\text{MTO-Nb}_2\text{O}_5$ for various olefins increase with the number of electron-rich groups on the double bond; also, *cis*-olefins show faster reaction rates than *trans*-olefins. New active peroxorhenium species are proposed on the basis of weak coordination of anions to the rhenium center due to a strong Brønsted acid on the surface of Nb_2O_5 . The reactivity difference is qualitatively explained according to frontier orbital interactions.

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References

- [1] W.A. Herrmann, D.W. Marz, J.G. Küchler, G. Weichselbaumer, R.W. Fischer, 1989, Germany, Hoechst AG, DE 3.902.357.
- [2] C.C. Romão, F.E. Kühn, W.A. Herrmann, Chem. Rev. 97 (1997) 3197–3246.
- [3] J.H. Espenson, Chem. Commun. (1999) 479–488.
- [4] W.A. Herrmann, R.W. Fischer, D.W. Marz, Angew. Chem., Int. Ed. 30 (1991) 1638.
- [5] W.A. Herrmann, R.W. Fischer, M.U. Rauch, W. Scherer, J. Mol. Catal. A: Chem. 86 (1994) 243.
- [6] W. Adam, C.M. Mitchell, Angew. Chem., Int. Ed. 35 (1996) 533.
- [7] J. Rudolph, K.L. Reddy, J.P. Chiang, K.B. Sharpless, J. Am. Chem. Soc. 119 (1997) 6189.
- [8] C. Coperet, H. Adolfsson, K.B. Sharpless, J. Chem. Soc., Chem. Commun. (1997) 1565.
- [9] G.S. Owens, M. Abu-Omar, Chem. Commun. (2000) 1165.
- [10] A.O. Bouh, J.H. Espenson, J. Mol. Catal. A: Chem. 200 (2003) 43–47.
- [11] W.-D. Wang, J.H. Espenson, J. Am. Chem. Soc. 120 (1998) 11335–11341.
- [12] I.E. Wachs, Y. Chen, J.-M. Jehng, I.E. Briand, T. Tanaka, Catal. Today 78 (2003) 13.
- [13] K.V. Chary, G. Kishan, T. Bhaskar, Chem. Commun (1999) 1399.
- [14] T.C. Watling, G. Deo, K. Seshan, I.E. Wachs, L.A. Lercher, Catal. Today 28 (1996) 139.
- [15] R.H.H. Smits, K. Seshan, J.R.H. Ross, A.P.M. Kentgens, J. Phys. Chem. 99 (1995) 9169.
- [16] Z. Zhu, J.H. Espenson, J. Mol. Catal. A: Chem. 121 (1997) 139.
- [17] R. Buffon, M.J.D.M. Jannini, A. Abras, J. Mol. Catal. A: Chem. 115 (1997) 173.
- [18] R. Buffon, M. Leconte, J.-M. Basset, R. Touroude, W.A. Herrmann, J. Mol. Catal. A 72 (1992) 139.
- [19] U. Biermann, W. Friedt, S. Lang, W. Lühs, G. Machmüller, J. Metzger, M.R. Klass, H.J. Schäffer, M.P. Schneider, Angew. Chem., Int. Ed. 39 (2000) 2206.
- [20] W.A. Herrmann, R.M. Kratzer, R.W. Fischer, Angew. Chem., Int. Ed. 36 (1997) 2652–2654.
- [21] R. Buffon, A. Auroux, F. Lefebvre, M. Leconte, A. Choplin, J.-M. Basset, W.A. Herrmann, J. Mol. Catal. A: Chem. 76 (1992) 287.
- [22] A. Al-Ajlouni, J.H. Espenson, J. Org. Chem. 61 (1996) 3969–3976.

- [23] A. Al-Ajlouni, J.H. Espenson, *J. Am. Chem. Soc.* 117 (1995) 9243–9250.
- [24] P. Gisdakis, S. Antonczak, S. Köstlmeier, W.A. Herrmann, N. Rösch, *Angew. Chem., Int. Ed.* 37 (1998) 2211.
- [25] F.E. Kühn, A.M. Santos, P.W. Roesky, E. Herdtweck, W. Scherer, P. Gisdakis, I.V. Yudanov, C.D. Valentin, N. Rösch, *Chem. Eur. J.* 12 (1999) 3603.
- [26] P. Giskakis, I.V. Yudanov, C.D. Valentin, N. Rösch, *Inorg. Chem.* 40 (2001) 3755.
- [27] D.V. Deubel, G. Frenking, H.M. Senn, J. Sundermeyer, *Chem. Comm* (2000) 2469.
- [28] T. Iizuka, K. Ofasawara, K. Tanabe, *Bull. Chem. Soc. Jpn.* 56 (1983) 2927.
- [29] J. Datka, A.M. Turek, J.M. Jheng, I.E. Wachs, *J. Catal.* 135 (1992) 186.
- [30] A. Ouquor, C. Coudrler, J.C. Vedrine, *J. Chem. Soc., Faraday Trans.* 89 (1993) 3151.
- [31] Z. Zhu, A. Al-Ajlouni, J.H. Espenson, *Inorg. Chem.* 35 (1996) 1408–1409.
- [32] C.P. Nicholas, H. Ahn, T.J. Marks, *J. Am. Chem. Soc.* 125 (2003) 4325.
- [33] H. Ahn, C.P. Nicholas, T.J. Marks, *Organometallics* 21 (2002) 1788.
- [34] H. Ahn, T.J. Marks, *J. Am. Chem. Soc.* 125 (2002) 7103.
- [35] W.A. Herrmann, J.G. Kuchler, J.K. Felixberger, E. Herdtweck, W. Wagner, *Angew. Chem., Int. Ed.* 27 (1988) 394.
- [36] N.D. Epiotis, R.L. Yates, F. Bernardi, *J. Am. Chem. Soc.* 97 (1975) 5961.
- [37] R. Boyd, S.L. Boyd, *J. Am. Chem. Soc.* 114 (1992) 1652.
- [38] P.R. Wells, *Prog. Phys. Org. Chem.* 6 (1968) 111.
- [39] R.D. Bath, M.N. Glukhovtsev, C. Gonzalez, *J. Am. Chem. Soc.* 120 (1998) 9902.
- [40] D.V. Deubel, *J. Org. Chem.* 66 (2001) 3790.