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((2-Hydroxynapthalen-1-yl)methylene)aniline derived Schiff base adducts of MTO: Synthesis and catalytic application

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ABSTRACT

Equimolar reactions of the derivatives of ((2-hydroxynapthalen-1-yl)methylene)aniline with methyltrioxorhenium (MTO) lead to complexes **1**–**4**, where MTO is coordinated via the oxygen of the former hydroxyl-group to MTO. The resulting complexes are very stable but not particularly catalytically active if no electron acceptor resides on the Schiff base. The electron withdrawing groups placed on the Schiff base ligand have the effect of increasing the catalytic activity but somewhat decrease the complex stability.

1. Introduction

Epoxides (Oxiranes), particularly ethylene and propene oxide, are key raw materials for a wide variety of chemicals such as glycols, glycol ethers, alkanolamines, and polymers. The simplest oxirane, ethylene oxide, is manufactured by vapor-phase oxidation of ethylene by air or oxygen over a heterogeneously supported silver catalyst at a multi million ton scale per year [1]. This method, however, is not applicable to propene, which gives low yields of propene oxide, owing to competing oxidation of allylic C–H bonds and leading to a variety of by-products. A method that has been applied for a long time for the synthesis of propylene oxide is the chlorhydrine route. This method, however, consumes a considerable amount of Cl_2 and has a very negative environmental impact. For the last decades significant research efforts both in industry and at universities have been dedicated to finding more efficient and less problematic synthetic pathways to propylene oxide and other valuable epoxides [2]. ARCO and Halcon described a homogeneous catalytic process for the synthesis of epoxides in the late 1960s [3] and since then many research groups concentrated on mechanistic aspects of these catalytic reactions and on finding improved catalysts [4–6]. Among the variety of efficient catalysts known today for olefin epoxidation are several organometallic oxides containing a metal in high oxidation state [7].

Well defined, highly active, inexpensive and stable catalysts, operating under environmentally benign conditions at room temperature and atmospheric pressure utilizing oxygen from air for epoxide generation would be the ideal means for industrial applications of olefin epoxidation, particularly in the synthesis of intermediates for high value added products such as pharmaceuticals. Unfortunately, such a stage has not yet been reached. The main obstacles in the way are currently a lack of mechanistic insight, high catalyst prices and insufficient catalyst stability and recyclability. However, several well-defined transition metal epoxidation catalysts already operate at room temperature and atmospheric pressure with impressively high turnover frequencies and good stability against "green solvents" such as water. Most prominent among them is methyltrioxorhenium (MTO) being available since quite recently from non-toxic, low price starting materials [8,9] and several organometallic and inorganic molybdenum and tungsten catalysts, employing comparatively cheap metals and being able to provide chiral ligand environments for chiral epoxidation [10,11] catalysis. The major drawback of most of these systems is their inability to utilize oxygen as an oxidizing agent, and, in part, the difficulty in immobilizing them on proper carrier materials or matrices and to obtain high epoxide selectivities [12].

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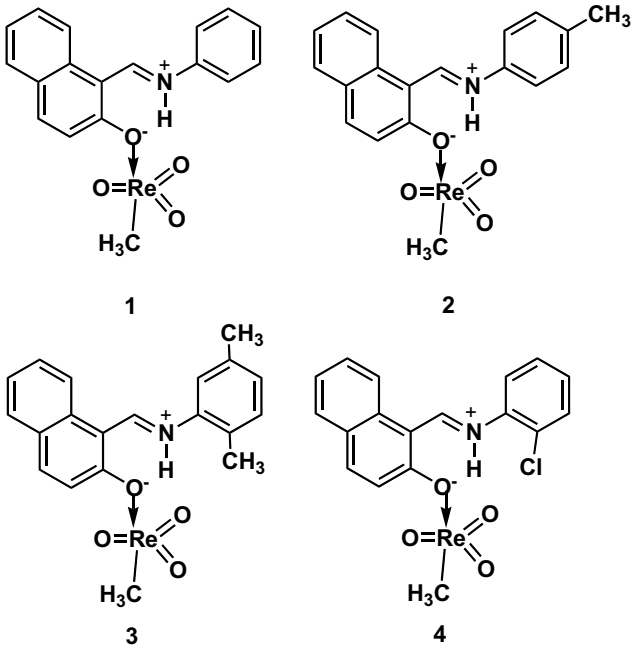
Selectivity was a major concern for the otherwise excellent MTO/H_2O_2 catalyst system for a couple of years. Due to the high Lewis-acidity of MTO and formation of water as a by-product from the oxidant hydrogen peroxide during the catalytic oxidation process, epoxide ring opening under diol formation took place at prolonged reaction times, being an unwanted side reaction. Addition of Lewis bases, such as triethylamine or quinuclidine did not lead to more satisfying results, since the diol formation was largely prevented at the expense of a great reduction of activity and catalyst life time [13]. However, it was found out later that aromatic Lewis base adducts of MTO show high activity in olefin epoxidation reactions, particularly when using the Lewis base in ca. 10-fold excess. Lower excesses usually reduce the activity or lead to more diol-byproducts [13]. It was also noted that aliphatic Lewis bases reduce the activity of MTO, regardless in which amount they are applied [14].

Recently, stable Schiff base adducts of MTO have been synthesized [15]. They show comparatively good catalytic activities in cyclooctene epoxidation and above-average stability under catalytic conditions. Moreover, an excess of ligand is not required for these compounds to be utilized in catalysis. In this work, ((2-hydroxynapthalen-1-yl)methylene)aniline derivatives are applied as ligands for MTO and their catalytic activity is examined.

2. Results and discussion

2.1. Synthesis and spectroscopic characterisation

In our previous work on Schiff base adducts of MTO it was noted that the electronic (and possibly the steric) constitution of the Schiff bases have a considerable influence on both the stability and the catalytic activity of the adducts [15]. However, stability and catalytic activity trends are unfortunately not necessarily going in the same direction. Another important issue is the accessibility of the applied Schiff bases, since complicated, low yielding, or expensive synthetic pathways are unwanted for almost any application. In this work, we utilize well established ((2-Hydroxynapthalen-1-yl)methylene)aniline derived Schiff bases as ligands for MTO [16]. Compounds **1**–**4** (Scheme 1) were synthesised by reacting MTO with the respective ligands, at room temperature in diethyl ether. It has to be emphasized that at lower temperatures than 0 °C no reaction takes place, whereas yields up to 80–90% are obtained in all examined cases when the reaction is executed at 20 °C. All products were re-crystallized from dichloromethane/*n*-hexane mixtures. Compounds **1**–**3** are stable and show no signs of decomposition, either in the solid state or in solution. They are stable in air and can be synthesized without further precautions. On the other hand, compound **4** is slightly moisture sensitive and needs to be stored at low temperatures in order to avoid decomposition.



Scheme 1. Formulae of compounds **1**–**4**.

The IR spectra of the compounds show some common features. The stretching bands of the iminic bonds, located at ca. 1600–1650 cm^{-1}, are shifted to higher wave numbers when compared to the free ligands in the case of the adducts due to electron delocalization. The geometry and coordination of the compounds can be inferred qualitatively when looking at the characteristic Re=O and Re–C stretching bands of the CH_3ReO_3 moiety (see Table 1).

On account of the expected complex symmetry (C_{3v}), a splitting of the asymmetric ReO_3 stretching band can be expected. This is seen in the case of compound **3**, but for complexes **1**, **2** and **4** only one single broad peak without clear substructure is observed. As the separation between the peaks is only ca. 10 cm^{-1} in the case of compound **3**, it is likely that the splitting is too small in these compounds to be resolved properly. Due to the donor capability of the ligands, which reduces somewhat the Re=O bond order, average symmetric and asymmetric Re=O stretching vibrations are red-shifted (20–30 cm^{-1}) in comparison to non-coordinated MTO. The same conclusion can be drawn from the observed blue shift changes of the iminic stretching vibrations. The difference between the coordinated and non-coordinated ligands is only ca. 10 cm^{-1} for the compounds **1**–**4**. As pointed out in our previous work [15] this displacement of the C=N stretching band can be explained in part by the formation of an intra molecular H bond between the N atom and the phenolic proton, which – according to the obtained IR data – seems to be quite weak in the case of adducts **1**–**4**.

The shift difference of 60–80 cm^{-1} between ν_s(Re=O) and ν_a(Re=O) indicates a trigonal-bipyramidal coordination, in contrast to the tetrahedral structure of free MTO [5a] (see Tables 1 and 2).

A selection of the NMR data of complexes **1**–**4** is shown in Table 3. On the first glance the ^1H NMR spectra show only slight changes from the non-coordinated MTO to Schiff base coordinated MTO. It should be noted, however, that in the *p*-CH_3 derivative the Re bound CH_3 protons display the strongest electron shift (compared to that of the protons of the Re–CH_3 group in free MTO), whereas in the case of the Cl-substituted Schiff base this shift is the weakest observed for the studied compounds. The ((2-hydroxynapthalen-1-yl)methylene)aniline derived Schiff base ligands are, as deduced from the obtained NMR data, coordinated to a slightly stronger extent than the previously reported Schiff bases utilized for MTO adducts. Within the four compounds examined in this work, compound **1** can be considered as a standard, non-substituted

Table 1
Characteristic vibrations of the MTO fragments (cm^{-1}) in **1**–**4**

MTO	1	2	3	4	Assignment
1368	1355	1366	1355	1356	CH_3, asym.def.
1205	1215	1217	1219	1217	CH_3, sym.def.
998	991	989	1006	992	ReO_3 sym. str.
965	930	926	940	925	ReO_3 asym.str.
			931		
567	566	567	558	553	ReC str.
981	961	958	959	959	ReO str. average
33	61	63	71	67	(ν_s–ν_a) ReO_3

Table 2
Selected IR data (cm^{-1}) for compounds **1–4**

Compound	Imine group	Phenolic OH group and coupled ring vibrations				
	$\nu_{(C=N)}$	β(OH)	$\nu_{(CX)}$	$\nu_{(CX)}$	$\nu_{(CX)}$	γ(OH)
$C_{17}H_{13}NO$	1621	1331	1251	1138	821 s	750vs
1	1629					
$C_{18}H_{15}NO$	1620	1327	1251	1083	815 m	742 m
2	1631					
$C_{19}H_{17}NO$	1619	1339	1257	1108	829 m	747 m
3	1632					
$C_{17}H_{12}NClO$	1622	1324	1257	1092	821 m	752vs
4	1615					

The respective vibrations of the non-coordinated, pure ligands are given for the sake of comparison.
Notation of vibrational modes: ν(C=N), C=N stretching; β(OH), hydrogen bonded OH in-plane deformation; ν(CX) substituent sensitive aromatic ring stretchings; γ(OH) phenolic out-of-plane vibrations.

Table 3
Selected ^1H and ^{13}C NMR data (ppm) of MTO complexes in $CDCl_3$

Compound	MTO–CH_3	
	$\delta(^1H)$	$\delta(^{13}C)$
MTO	2.67	19.03
1	2.59	19.46
2	2.50	19.88
3	2.58	19.26
4	2.62	19.09

compound; compounds **2** and **3,** which have donor substituents, lead in principle to a somewhat stronger coordination. Compound **4** bears an electron withdrawing ligand. The observed chemical shifts match that ligand pattern very well. It was expected that compound **4** would be both the least stable and most catalytically active compound. Both expectations turned out to be correct (*vide supra* for stability, *vide infra* for catalytic activity). In addition, the expected behaviour for compound **2** (i.e., to be the most stable and the least catalytically active amongst the examined complexes) was also fulfilled, as reflected in the NMR data.

As mentioned in a previous paper [15], the *trans* or *cis* arrangement of the Re bound CH_3 group with respect to the co-ordinating O-atom of the Schiff base ligand may be attributed to crystal packing effects in the solid state. Unfortunately, single crystal structures for complexes **1–4** could not be obtained. Nevertheless, ^{17}O NMR spectroscopy is a useful tool to examine the electron richness of the (terminal) oxygen atoms in solution. Axially coordinated oxo ligands are usually clearly distinguished by their chemical shift from equatorial oxo ligands, but these differences can often be seen only at low temperatures, since on the NMR time scale fast position changes of the oxo ligands take place [14,17]. A number of ^{17}O NMR experiments were carried out at different temperatures, using deuterated chloroform as solvent (see Table 4). The results show only one single signal in all cases for compounds **1–4**. Only a broadening of the ^{17}O signals at 223 K as it is usual at lower temperatures is observed.

The CI-MS spectra show, in all cases, the peaks of both MTO and the intact ligands. In addition, the molecular peak of the complete molecule can be seen in the case of complexes **1–3**. These observations are in good accord with the previously mentioned stabilities of the compounds, with complex **4** being the least stable. Similar fragmentation patterns have been observed and noted for MTO Lewis base adducts under the same conditions [13b,c].

2.2. Application in epoxidation catalysis

Compounds **1–4** were examined as catalysts for the epoxidation of cyclooctene, 1-octene and styrene with hydrogen peroxide. Further details of the catalytic reactions are given in Section 4. In the case of cyclooctene and 1-octene as substrates, no significant amounts of epoxide are formed in the absence of catalyst, and no by-products (such as diols) were detected during the course of the reaction. The catalyst:substrate:oxidant ratio was 1:100:200 in all cases, using mesitylene as internal standard. The time-dependent curves suggest first order kinetics.

Compounds **1–3** show low catalytic activity achieving yields not higher than 40% during the first 24 h with all examined substrates, not even with cyclooctene, being the most easy to oxidize. In contrast, complex **4** affords a 70% yield within 4 h for cyclooctene epoxide, more than 50% for styrene epoxide and 1-octene and reaches 100% within 24 h in all three examined substrate cases (Fig. 1). These results match well with the spectroscopic data of the complexes presented above and show that the least electron donating ligand (complex **4**) leads to the weakest complex, but also to the most active catalyst. Stronger donating ligands lead to more stable catalysts (**1–3**), which are, however, less active. This can be explained by the influence of the ligands on the Lewis acidity of the Re atom and the adjacent terminal ligands. If the Lewis acidity of the metal is reduced, the formation of catalytically active mono- and bisperoxo complexes is hampered. Additionally, a decrease in the electron deficiency of the peroxo-oxygen atoms makes the catalyst less prone to a nucleophilic attack by an olefin [13b]. The steric bulk of the Schiff base ligand seems to be of minor importance in comparison to the donor/acceptor capabilities. Hence the Re–O (Schiff base) bond is strengthened, if the Schiff base can donate more electron density and weakened, if it gives little density. While complexes **1–4** are not as active as non-coordinated MTO in epoxidation catalysis, they show an increased selectivity towards epoxides. It should be pointed out that

Table 4
Temperature-dependent ^{17}O NMR spectroscopic data for complexes **1–4** in chloroform

Temperature (°C)	**1**		**2**		**3**		**4**	
	δ (ppm)	$\Delta\nu_{1/2}$ (Hz)	δ (ppm)	$\Delta\nu_{1/2}$ (Hz)	δ (ppm)	$\Delta\nu_{1/2}$ (Hz)	δ (ppm)	$\Delta\nu_{1/2}$ (Hz)
−50	830	90	833	74	830	75	829	88
−20	827	37	828	24	827	24	827	35
0	827	36	827	16	826	17	826	29
20	827	25	827	12	827	14	826	20

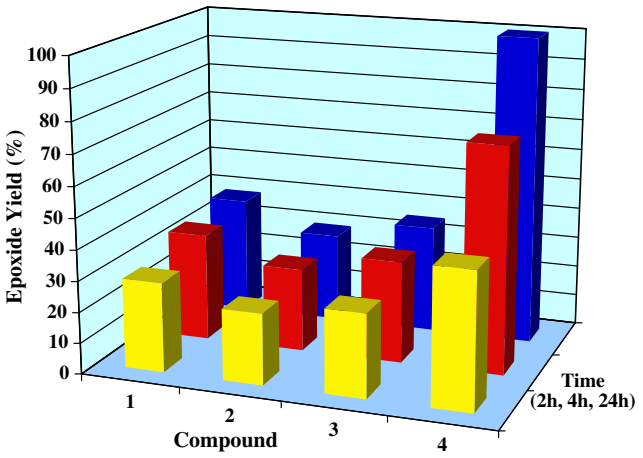


Fig. 1. Yield of cyclooctene epoxidation after 2 h, (yellow bars) 4 h (red bars), and after 24 h (blue bars) in the presence of catalytic amounts of the complexes **1**–**4**. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

excess of Schiff base ligand leads to catalyst decomposition and loss of catalytic activity. This is in contrast to the behaviour of Lewis base adducts of MTO, where pyridine based ligands significantly accelerate the catalytic reactions when applied in larger excess [13].

3. Conclusions

Selected ((2-hydroxynapthalen-1-yl)methylene)aniline derived Schiff base ligands react with MTO, yielding 1:1 adducts. The obtained complexes resemble in principle the previously described (salicylidene)aniline Schiff base ligands but are in general more stable (also under CI-MS conditions) and can be handled in air for hours without problem, with the exception of the compound bearing a chloro substituent in ortho position. Despite being the least stable of the examined compounds, the latter complex displays the highest catalytic activity in olefin epoxidation. The electron donor capability of the Schiff base ligands is also reflected in the NMR spectra of the MTO moiety. Despite the seemingly weak coordination of the Schiff base ligand, the latter has a quite significant influence on both the stability and the catalytic performance of the resulting complex. More work, whether this observation can be regarded as a general rule for MTO Schiff base complexes is under work in our laboratories.

4. Experimental

4.1. Synthesis and characterisation

All preparations and manipulations were performed using standard Schlenk techniques under an argon atmosphere. However, in the case of **1**–**3** the synthesis can be carried out under air without problems. Solvents were dried by standard procedures (*n*-hexane and Et_2O over Na/benzophenone; CH_2Cl_2 over CaH_2), distilled under argon and kept over molecular sieves. Elemental analyses were performed with a Flash EA 1112 series elemental analyser. ^1H, ^{13}C NMR and ^{17}O NMR were measured in $CDCl_3$ with a Varian 270 and 400 or a 400 MHz Bruker Avance DPX-400 spectrometer. IR spectra were recorded with a Perkin–Elmer FT-IR spectrometer using KBr pellets as the IR matrix. CI mass spectra (isobutene as CI gas) were obtained with a Finnigan MAT 90 mass spectrometer. Catalytic runs were monitored by GC methods on a Varian CP-3800 instrument equipped with a FID and a VF-5 ms column. The Schiff base ligands were prepared as described previously [16].

Compounds **1**–**4** were prepared as follows: A solution of $[(CH_3)ReO_3]$ (0.15 g, 0.6 mmol) in diethyl ether (5 mL) was added drop wise to an equally concentrated solution of ligand (0.6 mmol) in diethyl ether (5 mL) whilst stirring at room temperature. After 20–30 min the yellow-orange solution-mixture was dried under oil pump vacuum and the orange precipitate recrystallized under CH_2Cl_2/hexane.

1: Yield: 82%. ^1H NMR (400 MHz, $CDCl_3$, rt, ppm): δ = 15.46 (d, $^3J_{(H-H)}$ = 3.2, 1H, C–N^+–H), 9.31 (d, $^3J_{(H-H)}$ = 3.7, 1H, CH=N), 8.1–7.1 (m, 11H, aryl), 2.59 (s, 3H, CH_3–MTO); ^{13}C NMR (100.28 MHz, $CDCl_3$, rt, ppm): δ = 171.26 (C–O^-), 154.13 (CH=N), 144.61, 136.90, 129.71, 128.14, 126.56, 123.55, 122.51, 120.12, 118.74, 108.70 (aryl-C), 19.46 (CH_3–MTO); IR (KBr, ν [cm^{-1}]): see Tables 1 and 2; CI-MS (70 eV) *m*/*z*: 497.06 [M^+], 250.9 [M^+-MTO], 248.9 [M^+-L]; Anal. Calc. for $C_{18}H_{16}NO_4Re$: C, 43.54; H, 3.25; N, 2.82. Found: C, 43.84; H, 3.24; N, 2.81%.

2: Yield: 80%. ^1H NMR (400 MHz, $CDCl_3$, rt, ppm): δ = 15.49 (d, $^3J_{(H-H)}$ = 4.2, 1H, C–N^+–H), 9.23 (d, $^3J_{(H-H)}$ = 4.2, 1H, CH=N), 8.1–7.0 (m, 10H, H-aryl), 2.50 (s, 3H, CH_3–MTO), 2.38 (s, 1H, Ph–CH_3); ^{13}C NMR (100.28 MHz, $CDCl_3$, rt, ppm): 171.87 (C–O^-), 153.72 (CH=N), 141.33, 137.19, 136.66, 133.31, 130.29, 129.37, 128.10, 127.06, 123.43, 122.69, 119.77, 118.62 (aryl-C), 70.57, 26.48, 20.99 (CH_3–Ph), 19.88 (CH_3–MTO); IR (KBr, ν [cm^{-1}]): see Tables 1 and 2; CI-MS (70 eV) *m*/*z*: 513.1 [M^+], 262.1 [M^+-MTO], 251.0 [M^+-L]; Anal. Calc. for $C_{19}H_{18}NO_4Re$: C, 44.70; H, 3.55; N, 2.74. Found: C, 45.07; H, 3.53; N, 2.69%.

3: Yield: 94%. ^1H NMR (270 MHz, $CDCl_3$, rt, ppm): δ = 15.72 (d, $^3J_{(H-H)}$ = 5.6, 1H, C–N^+–H), 9.26 (d, $^3J_{(H-H)}$ = 5.8, 1H, CH=N), 8.1–7.0 (m, 9H, H-aryl), 2.58 (s, 1H, CH_3–MTO), 2.45–2.42 (s, 2H, Ph–CH_3); ^{13}C NMR (100.28 MHz, $CDCl_3$, rt, ppm): δ = 172.51 (C–O^-), 153.13 (CH=N), 137.15, 130.96, 129.39, 128.11, 127.24, 123.44, 122.98, 118.66, 117.72, 108.71 (aryl-C), 21.15, 17.70 (CH_3–Ph), 19.26 (CH_3–MTO); IR (KBr, ν [cm^{-1}]): see Tables 1 and 2; CI-MS (70 eV) *m*/*z*: 527.1 [M^+] 276.1 [M^+–MTO], 250.9 [M^+–L]; Anal. Calc. for $C_{20}H_{20}NO_4Re$: C, 45.79; H, 3.84; N, 2.67. Found: C, 45.69; H, 3.76; N, 2.63%.

4: Yield: 80%. ^1H NMR (400 MHz, $CDCl_3$, rt, ppm): δ = 15.40 (d, $^3J_{(H-H)}$ = 3.2, 1H, C–N^+–H), 9.39 (d, $^3J_{(H-H)}$ = 3.2, 1H, CH=N), 8.1–7.1 (m, 10H, H-aryl), 2.62 (s, 1H, CH_3–MTO); ^{13}C NMR (100.28 MHz, $CDCl_3$, rt, ppm): 168.97 (C–O^-), 155.60 (CH=N), 143.23, 136.83, 133.09, 130.38, 129.43, 128.16, 127.88, 127.50, 127.14, 123.73, 121.71, 118.96, 118.67, 109.22 (C-aryl), 19.09 (CH_3–MTO); IR (KBr, ν [cm^{-1}]): see Tables 1 and 2; CI-MS (70 eV) *m*/*z*: 282.0 [M^+–MTO], 250.9 [M^+–L]; Anal. Calc. for $C_{18}H_{15}ClNO_4Re$: C, 40.72; H, 2.85; N, 2.64; Cl, 6.68. Found: C, 40.53; H, 2.84; N, 2.44; Cl, 6.78%.

4.2. Catalytic reactions

cis-Cyclooctene (800 mg, 7.3 mmol), 1.00 g of mesitylene (internal standard), H_2O_2 (30% aqueous solution; 1.62 ml, 14.6 mmol) and 1 mol% (73 μmol) of compounds **1**–**4** were mixed, diluted in 30 ml of CH_2Cl_2, added to the reaction vessel under air at room temperature and the reaction was started by adding H_2O_2. The course of the reactions was monitored by quantitative GC analysis. Samples were taken at regular time intervals and treated with a catalytic amount of $MgSO_4$ and MnO_2 to remove water and to destroy the unreacted peroxide. The resulting slurry was filtered and the filtrate injected onto a GC column. The conversion of cyclooctene and the formation of cyclooctene oxide were calculated from calibration curves (r^2 = 0.999) recorded prior to the reaction.

The reactions with 1-octene and styrene were performed in the same way.

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References

[1] P.A. Kilty, W.M.H. Sachtler, Catal. Rev. 10 (1974) 1.
[2] (a) H. Adolfsson, J.E. Bäckvall (Eds.), Modern Oxidation Methods, Wiley-VCH, Weinheim, 2004. p. 21;
(b) A.K. Yudin (Ed.), Aziridines and Epoxides in Organic Synthesis, Wiley-VCH, Weinheim, 2006.
[3] (a) J. Kollar (Halcon) US 3.350.422, US 3.351.635, 1967;
(b) M.N. Sheng, G.J. Zajaczek, (ARCO) GB 1.136.923, 1968;
(c) R. Coltan, I.B. Tomkins, Austr. J. Chem. 18 (1965) 447.
[4] (a) E.O. Fischer, S. Vigoureux, Chem. Ber. 91 (1958) 1342;
(b) E.O. Fischer, K. Ulm, H.P. Fritz, Chem. Ber. 93 (1960) 2167;
(c) M. Cousins, M.L.H. Green, J. Chem. Soc. (1963) 889.
[5] (a) W.A. Herrmann, F.E. Kühn, Acc. Chem. Res. 30 (1997) 169;
(b) D.V. Deubel, G. Frenking, P. Gisdaks, W.A. Herrmann, N. Rösch, J. Sundermeyer, Acc. Chem. Res. 37 (2004) 645;
(c) A.O. Chong, K.B. Sharpless, J. Org. Chem. 42 (1977) 1587;
(d) M.N. Sheng, J.G. Zajacek, J. Org. Chem. 35 (1970) 1839;
(e) R.A. Sheldon, J.A. van doorn, J. Catal. 31 (1973) 427;
(f) R.A. Sheldon, J.A. van Doorn, C.W.A. Schram, J. de Jong, J. Catal. 31 (1973) 438.
[6] (a) R.A. Sheldon, Recueil Trav. Chim. 92 (1973) 253;
(b) W.R. Thiel, J. Mol. Catal. A – Chem. 117 (1997) 449;
(c) G. Wahl, D. Kleinhenz, A. Schorm, J. Sundermeyer, R. Stowasser, C. Rummey, G. Bringmann, Chem. Eur. J. 5 (1999) 3237;
(d) R. Poli, Chem. Eur. J. 10 (2004) 332;
(e) P. Chaumette, H. Mimoun, L. Saussine, J. Organomet. Chem. 250 (1983) 291;
(f) M.K. Trost, R.G. Bergman, Organometallics 10 (1991) 1172.
[7] (a) F.E. Kühn, A.M. Santos, M. Abrantes, Chem. Rev. 106 (2006) 2455;
(b) C.C. Romão, F.E. Kühn, W.A. Herrmann, Chem. Rev. 97 (1997) 3197.
[8] W.A. Herrmann, A.M.J. Rost, J.K.M. Mitterpleininger, N. Szesni, W. Sturm, R.W. Fischer, F.E. Kühn, Angew. Chem., Int. Ed. 46 (2007) 7901.
[9] E. Tosh, H.K.M. Mitterpleininger, A.M.J. Rost, D. Veljanovski, W.A. Herrmann, F.E. Kühn, Green Chem. 12 (2007) 1296.
[10] F.E. Kühn, J. Zhao, W.A. Herrmann, Tetrahedron Asym. 16 (2005) 3469.
[11] K.R. Jain, W.A. Herrmann, F.E. Kühn, Coord. Chem. Rev. 252 (2008) 556.
[12] K.R. Jain, F.E. Kühn, J. Organomet. Chem. 692 (2007) 5532.
[13] (a) J. Rudolph, K.L. Reddy, J.P. Chiang, K.B. Sharpless, J. Am. Chem. Soc. 119 (1997) 6189;
(b) F.E. Kühn, A.M. Santos, P.W. Roesky, E. Herdtweck, W. Scherer, P. Gisdakis, I.V. Yudanov, C. di Valentin, N. Rösch, Chem. Eur. J. 5 (1999) 3602;
(c) P. Ferreira, W.-M. Xue, E. Bencze, E. Herdtweck, F.E. Kühn, Inorg. Chem. 40 (2001) 5834.
[14] W.A. Herrmann, F.E. Kühn, M.U. Rauch, J.D.G. Correia, G. Artus, Inorg. Chem. 34 (1995) 2914.
[15] M.-D. Zhou, J. Zhao, J. Li, S. Yue, C.-N. Bao, J. Mink, S.-L. Zang, F.E. Kühn, Chem. Eur. J. 13 (2007) 158.
[16] (a) J. Lopez, S. Liang, X.R. Ru, Tetrahedron Lett. 39 (1998) 4199;
(b) D.M. Boghaei, S. Mohebi, J. Mol. Catal. A. Chem. 179 (2002) 41;
(c) B.-B. Lin, Y.-Q. Qiu, Z.-M. Su, S.-L. Sun, J.-K. Feng, Chem. J. Chinese Univ. 22 (2001) 1551.
[17] W.A. Herrmann, F.E. Kühn, P.W. Roesky, J. Organomet. Chem. 485 (1995) 243.