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Benzimidazolic complexes of methyltrioxorhenium(VII): Synthesis and application in catalytic olefin epoxidation

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ABSTRACT

Seven new Lewis base adducts of methyltrioxorhenium(VII) (MTO) with the general formula $CH_3ReO_3 \cdot L$ (L = bidentate benzimidazolic ligands, namely (L = 2-(2-Pyridinyl)-1H-benzimidazole, 5-methyl-2-(2-pyridyl)benzimidazole, 5-Chloro-2-(2-pyridyl)benzimidazole, 2-(2-Pyridyl)-1H-imidazo-[4,5-b]-pyridine, 2-(2-Quinolyl)benzimidazole, 2-(5-methyl-1H-benzimidazol-2-yl)-quinoline, and 2-(5-chloro-1H-benzimidazol-2-yl)-quinoline)) were prepared. All the complexes were characterized by IR, ^1H, ^{13}C NMR, MS and elemental analysis as well as tested as catalysts for olefin epoxidation using 35% aqueous hydrogen peroxide as oxidant under mild condition. The influence of different ligand concentrations was also examined. The results show that the complexes are highly selective in olefin epoxidation and good yields can be obtained when excess ligand is applied.

1. Introduction

Epoxides are versatile starting materials for value added products such pharmaceuticals, flavor and fragrance molecules [1–4]. A broad variety of catalysts for olefin epoxidation has been described over the years with organometallic complexes being very efficient as catalysts for the synthesis for fine chemicals and for sophisticated organic substrates [5–11]. Certainly one of the most widely applied and well examined among them is methyltrioxorhenium(VII) (MTO) [12–14]. MTO utilizes hydrogen peroxide as oxidizing agent producing only water as by-product, making such reaction environmentally benign [15–20]. A major drawback of this system is the Lewis acidity of the catalyst in the presence of water: it promotes ring opening reactions, leading to a mixture of epoxide and diol instead of forming only one product with high selectivity [12,13]. Although systems containing Lewis bases have been examined early with respect to their ability to buffer the Lewis acidity without reducing the catalyst activity, all these early attempts did not prove successful [21–23].

In the late 1990s Sharpless et al. discovered that a significant excess of aromatic N-coordinating Lewis bases is needed to get high selectivity towards epoxide without reduction of catalyst activity or lifetime [24–27]. The effect was explained by shifting the equilibrium between free and Lewis base coordinated MTO towards the latter, maintaining the interaction in the catalytically active species [28,29]. Although numerous N-bases have been described [21–32], adducts without N-donor functionalities and nevertheless leading to good selectivity when applied with the MTO/H_2O_2-system remained the exception [33–39].

Benzimidazole is a typical heterocyclic ligand with nitrogen as the donor atom. In the case of 2-(2-pyridinyl)-1H-benzimidazole, the bidentate ligand can be described as electron-donating due to the two nitrogen atoms of the benzimidazole and pyridine moieties. Studies about the coordination chemistry of benzimidazolic ligands have been carried out with a variety of metal ions [40–42], however, MTO complexes containing benzimidazole based ligands have not been described until now. In this paper the synthesis, characterization and catalytic application of bidentate MTO benzimidazole adducts are described.

2. Results and discussion

2.1. Synthesis and spectroscopic characterization

The addition of one equivalent of MTO to the bidentate N-donor benzimidazolic derivatives in dichloromethane at room temperature leads to the formation of the corresponding MTO-Lewis-base complexes **1**–**7** (see Scheme 1), which can be easily isolated as a yellow or orange solids in good yields. These bidentate complexes have a good stability both in solid state and in solution at the room temperature. In the solid state, all the complexes are not very sensitive to air, but slightly sensitive to moisture. Therefore,

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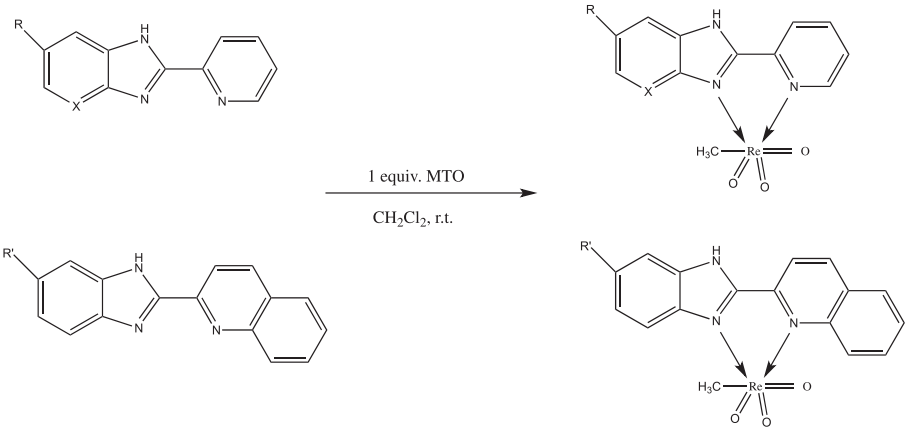


R=H, X=C (**1**); R=Me, X=C (**2**); R=Cl, X=C (**3**); R=H, X=N (**4**);
R'=H (**5**); R'=Me (**6**); R'= Cl (**7**)

Scheme 1. Synthesis of MTO salen complexes **1**–**7**.

a water-free atmosphere is needed to preserve the complexes over prolonged periods of time.

The IR spectra of the complexes **1**–**7** show strong symmetric Re=O stretching vibrations in the region of 946–958 cm^{-1} whilst the asymmetric Re=O stretching vibration lies between 919 and 929 cm^{-1} (see Table 1). The Re=O bands of the complexes **1**–**7** are significantly red-shifted compared to the vibrations (ν sym = 992 cm^{-1}, ν asym = 965 cm^{-1}) of MTO alone [43]. The vibration differences reflect the donating capacity of the bidentate benzimidazolic ligands. The additional electron density originating from the ligands significantly reduce the strength of the Re=O bonds.

The main vibrational frequencies of the benzimidazolic ring, namely the ν(N–H), ν(C=C), ν(C=N) vibrations of pyridine and imidazole, as well as the δ(C–N) and δ(C–H) benzimidazolic ring out of plane vibrations are observed [44,45]. In all IR spectra of compounds **1**–**7** peaks originating from these vibrations are evident (Table 2). Interestingly, the bands are shifted towards higher wave numbers as compared with the position in the free ligands. These results are indicative of ligand coordination through the benzimidazolic nitrogen. Moreover, the vibration of (N–H) bands of the benzimidazolic ligands are seen in the range of 3000–3400 cm^{-1} as a very broad band, and the ligands show characteristic pyridine and imidazole C=N frequencies in the range of 1563–1571 cm^{-1} and 1590–1597 cm^{-1}. It is noteworthy that the sharp band between 1454 and 1510 cm^{-1} is due to the stretching vibration of aromatic C=C. Another sharp band between 736 and 748 cm^{-1} can be assigned to the out-of-plane C–H bending vibrations of the di- and tri-substituted benzene ring [46].

The strong band around 1300–1320 cm^{-1} in the spectra of the ligands is shifted towards higher energy and splitted upon chelation, indicating coordination through the pyridine-nitrogen atom [47,48]. In case of complex **1**, the split band appears at 1323 cm^{-1} and 1301 cm^{-1} whereas it is at 1312 cm^{-1} in the spectrum of L1 as a strong band. In addition to this, differences are observed in the band character due to the effect of metal complexation. For example, the medium strong (C=N) bands are changed to a shoulder or weak bands in some complexes [49].

Table 1
Characteristic IR vibrations of CH_3ReO_3 fragments (cm^{-1}) in **1**–**7**.

MTO	**1**	**2**	**3**	**4**	**5**	**6**	**7**	Assignment
992	943	946	950	950	958	956	955	ReO_3 sym str
965	919	922	925	926	929	929	925	ReO_3 asym str

Selected ^{1}H NMR spectroscopic data of the benzimidazolic ligands and the MTO complexes are shown in Table 3. Compared to the spectra of the non-coordinated MTO, the proton signals originating from the Re–CH_3 of the MTO complexes **1**–**4** are shifted to higher magnetic field as reported in the literature [50,51]. With regard to the MTO complexes **5**–**7**, the proton signals from the Re–CH_3 group are not shifted much due to the influence of the quinoline ring. The magnitude of the shift is directly related to the electron-donating capability of the ligands. For example, relative to MTO itself, complexes **3** bearing an electron-withdrawing chlorine atom on the phenyl moiety shows a chemical shift of the methyl signal from 1.90 ppm to 1.76 ppm. However, in the case of complex **2**, which has a methyl group on the phenyl moiety, the ^{1}H shift changes from 1.90 ppm to 1.55 ppm. Furthermore, the signals of the N–H group on the imidazole ring of complexes **1**, **2**, **3**, **4** and **7** are slightly shifted to lower field compared to free benzimidazolic ligands. The N–CH vibration in the pyridine ring is also slightly shifted to a lower field in these cases.

2.2. Application as epoxidation catalysts

Compounds **1**–**7** were examined as catalysts for the epoxidation of cyclooctene with 35% H_2O_2 as oxidant in dichloromethane at room temperature. A catalyst: oxidant: substrate ratio of 1:100:50 was applied in all experiments. The results are summarized in Table 4. Among all the catalysts, compound **4** appears to be the best for epoxidation of *cis*-cyclooctene. The yield reaches 99% and the

Table 2
Selected IR spectroscopic data of ligands and MTO complexes.

Compound	ν (N–H) (cm^{-1})	ν (C=N) (cm^{-1})	ν (C=C) (cm^{-1})	δ (C–N) (cm^{-1})	δ (C–H) (cm^{-1})
L1	3042	1590, 1564	1465	1439, 1397	740
1	3078	1608, 1591	1497	1457, 1440	745
L2	3056	1590, 1568	1458	1441, 1396	744
2	3075	1607, 1593	1547	1490, 1452	749
L3	3050	1593, 1569	1454	1443, 1400	736
3	3068	1602, 1589	1547	1491, 1442	752
L4	3060	1595, 1568	1465	1446, 1414	741
4	3087	1589	1539	1481, 1454	760
L5	3043	1595, 1571	1496	1442, 1413	740
5	3074	1596	1510	1475, 1456	761
L6	3048	1597, 1566	1508	1447, 1405	748
6	3063	1603, 1594	1553	1480, 1428	748
L7	3055	1597, 1563	1497	1442, 1412	741
7	3062	1602, 1593	1506	1471, 1428	756

Table 3
Selected ^1H and ^{13}C NMR spectroscopic data for complexes **1**–**7** in d^6-DMSO.

	N–CH(Py) ligand, ^1H δ [ppm]	N–CH(Py) complex, ^1H δ [ppm]	NH ligand ^1H δ [ppm]	NH complex ^1H δ [ppm]	Re–CH_3, ^1H δ [ppm]	Re–CH_3, ^{13}C δ [ppm]
MTO					1.90	25.39
1	8.74	8.77	13.09	13.29	1.77	25.79
2	8.73	8.80	12.96	13.53	1.55	25.90
3	8.75	8.77	13.32	13.46	1.76	25.58
4	8.78	8.80	13.52	13.75	1.87	25.52
	8.41	8.78				
5	–	–	13.20	13.19	1.91	25.42
6	–	–	13.06	13.03	1.91	25.43
7	–	–	13.20	13.35	1.91	25.42

TOF is 236 h^{-1} (Entry 4). The other complexes show only moderate or low conversions during the first hour and no significant improvement even after 24 h (Entries 1–3, 5–7). The better performance of **4** may be due to its enhanced stability due to electron delocalization (Scheme 2) and its stronger Lewis basicity.

On the other hand, this poor conversion may be also due to the presence of NH groups in the benzimidazolic ligands [52]. They may interfere with the catalytic cycle by forming hydrogen bonds with produced H_2O during the reaction. In summary, the strong coordination capacity of the di-nitrogen benzimidazolic ligands can slightly increase the epoxidation selectivity but reduce the conversion of the epoxidation reaction. A similar situation is also known of other related literature described systems [53,54].

MTO complex **4** was also tested as catalyst for the epoxidation of various other olefins including cyclic olefins and long-chain olefins with H_2O_2 as oxidant. The results are given in Table 5. It has to be noted here that 1-octene is readily epoxidized into its epoxide the yield being 99% (Entry 2). For trans-β-methylstyrene (Entry 3), limonene (Entry 4) and (+)-camphene (Entry 5), usually more challenging substrates for epoxidation, still relatively high yields (>70%) can be obtained (Entries 3–5).

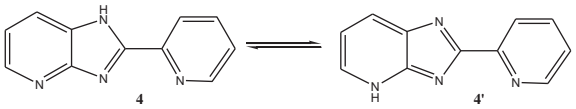
2.3. Influence of the ligands concentration

L1 was used to investigate the influence of the ligands concentration on the epoxidation reaction. The epoxidation results in the first hour are summarized in Fig. 1. Application of free MTO (line d) leads to a yield 88% after 1 h reaction time and a TOF of 280 h^{-1}. Compared to this, the epoxide yield was only 25%, 15% and 28% after 1 h with no further changes even after 24 h when the molar rate of L1:MTO was 0.5:1, 1:1 and 2:1(line a, b, c). The activity of the catalytic system increased when the ratio of L1:MTO was raised to 10:1. The reaction displayed a TOF of nearly 700 h^{-1} and a yield of 57% after 5 min and reached to 98% after 1 h (line e). With higher ligands concentrations, the epoxide yield slightly increased to 63% and 76% after 5 min reaction time and reached almost 100% after

Table 4
Epoxidation of *cis*-cyclooctene with different catalyst using H_2O_2 as oxidant.[a]

Entry	Catalyst	Yield[b] (%)	Selectivity[b] (%)	TOF[c] (h^{-1})
1	**1**	29	99	137
2	**2**	23	99	149
3	**3**	34	99	211
4	**4**	99	99	236
5	**5**	25	99	132
6	**6**	31	99	176
7	**7**	33	99	152

[a] Reaction condition: *cis*-cyclooctene (2 mmol); H_2O_2 (35%)(4 mmol), catalyst (2 mol%), CH_2Cl_2 (1.2 mL) at room temperature, $t = 1$ h.
[b] Yield and selectivity are calculated based on GC analysis.
[c] Determined after 5 min.



Scheme 2. Resonance structures **4** and **4′**.

1 h with a TOF of *ca.* 750 h^{-1} and *ca.* 920 h^{-1} when the molar ratio of L1:MTO was raised to 20:1 and 50:1 (line f and g). The results show that large excesses of benzimidazolic ligands lead to higher catalytic activity for olefin epoxidation. This observation is in contrast to previous observations with modentate pyridine-derived ligands, where the activity and yield did not change significantly when ratios higher than 1:10 (MTO: Lewis base) were reached. The reason for the observed behavior may be as follows: the NH groups in the benzimidazolic ligands may form hydrogen bonds with the oxidant leading to an activity decrease. The amount of active species present, however, increases with increasing amounts of the ligand due to a favorable shift of the equilibrium. The large excesses of the ligands help to maintain the activity by providing the catalytically active species in a significant enough concentration. Furthermore, the strong electron-donating ability of the ligand may contribute to an acceleration of the formation of the active species, leading to a better catalytic activity. Calculations are under way to prove these assumptions.

3. Conclusions

Several bidentate N-donor benzimidazolic adducts of MTO were synthesized, characterized and applied for catalytic olefin epoxidation using H_2O_2 as oxidant in CH_2Cl_2 at room temperature. The benzimidazolic MTO compounds show good stability and can be exposed to air for several days. Most complexes exhibit good selectivity but relatively low activity. A large excess of the benzimidazolic ligands however, is able to increase the catalytic activity significantly.

4. Experimental

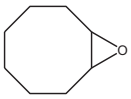
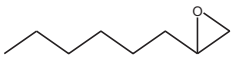
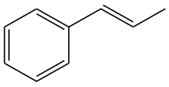
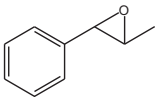
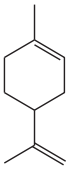
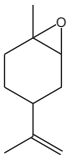
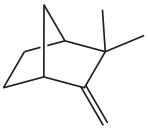
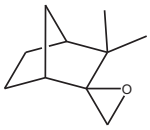
4.1. Materials

All preparation and manipulations were performed using standard Schlenk techniques under an Argon atmosphere. All the chemicals for syntheses were obtained commercially and used without further purification. Solvents were dried by standard procedures (*n*-hexane over Na/benzophenone; CH_2Cl_2 over CaH_2), distilled under argon and used immediately or kept over 4 Å molecular sieves. Elemental analyses were performed with a Flash EA 1112 series elemental analyzer. ^1H and ^{13}C NMR were measured in d^6-DMSO with a mercury-VX 300 spectrometer and a 400-MHz Bruker Avance DPX-400 spectrometer. IR spectra were recorded using a Perkin Elmer FT-IR spectrometer with KBr pellets as the IR matrix. CI-MS spectra were measured on a Finnigan MAT 90 mass spectrometer. Catalytic runs were monitored by GC methods on a Hewlett–Packard instrument HP 5890 Series II equipped with a FID, a Supelco column Alphadex 120 and a Hewlett–Packard integration unit HP 3396 Series II. MTO was synthesized according to the literature procedures [16,17].

4.2. Synthesis of the ligands

The ligands L1-L7 were prepared according to literature procedures [55]. All the ligands were characterized by IR, ^1H NMR and elementary analysis.

Table 5
Epoxidation of different olefins with complex **4** as catalyst using H_2O_2 as oxidant in CH_2Cl_2.[a]

Entry	Substrate	Product	Time (h)	Conversion (%)[b]	Yield (%)[b]
1			1	99	99
2			24	99	99
3			4	96	96
4			3	73	73
5			0.5	77	77

[a] Reaction condition: olefins (2 mmol); H_2O_2 (35%)(4 mmol), catalyst **4** (2 mol%), CH_2Cl_2 (1.2 mL) at room temperature.
[b] The yield and selectivity are calculated by GC analysis.

4.3. Synthesis of MTO complexes

All MTO complexes were synthesized according to a general procedure: a solution of MTO (0.05 g, 0.2 mmol) in CH_2Cl_2 (2 mL) was drop-wise added to an equally concentrated solution of ligand (L1–L7) in CH_2Cl_2 (5 mL) under stirring at room temperature. For **1**, **2**, **5** a yellow precipitate formed rapidly. The precipitate was isolated by filtration, washed with *n*-hexane and dried under reduced pressure. For **3**, **4**, **6**, **7**, the reaction mixture was stirred for 1 h at room temperature before removing the solvent in vacuum. The remaining solid was washed with *n*-hexane twice and dried under reduced pressure.

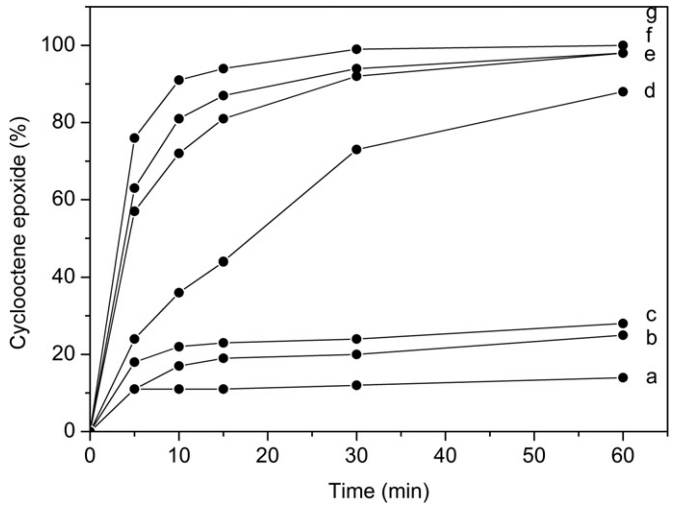


Fig. 1. Influence of the ligand concentration on the yield, L1:MTO = 1:1 (a), 0.5:1 (b), 2:1 (c), 10:1 (e), 20:1 (f), 50:1 (g), MTO (d).

Compound **1**: yellow powder, Yield: 85%. $C_{13}H_{12}N_3O_3Re$ (445), elemental analysis: Theory (C: 35.13; H: 2.72; N: 9.45), Found (C: 35.38; H: 2.72; N: 9.48); IR (KBr, ν cm^{-1}):3078, 1608, 1591, 1457, 1440, 943, 919, 745; ^1H NMR (d^6-DMSO, 400 MHz, r.t.): δ (ppm) = 13.29 (1H, s, NH), 8.77, 8.76 (1H, d, Py), 8.36, 8.37 (1H, d, Py), 8.04, 8.06, 8.07 (1H, t, Py), 7.66 (2H, s, Ph), 7.55, 7.56 7.57 (1H, t, Py), 7.26–7.28 (2H, m, Ph), 1.77 (3H, s, MTO–CH_3); ^{13}C NMR (d^6-DMSO, 100 MHz, r.t.): δ (ppm) = 150.45, 149.64, 147.49, 138.73, 126.80, 123.69, 122.47, 116.91, 26.79; MS (CI): m/z = 430.8 $[M - CH_3]^+$, 195.8 $[M - MTO]^+$, 234.8 $[ReO_3]^+$.

Compound **2**: yellow powder, Yield: 83%. $C_{14}H_{14}N_3O_3Re$ (459), elemental analysis: Theory (C: 36.67; H: 3.08; N: 9.16), Found (C: 37.22; H: 3.09; N: 9.25); IR (KBr, ν cm^{-1}): 3075, 1607, 1593, 1490, 1452, 946, 922, 749; ^1H NMR (d^6-DMSO, 400 MHz, r.t.): δ (ppm) = 13.53 (1H, s, NH), 8.80, (1H, s, Py), 8.39, 8.38 (1H, d, Py), 8.15–8.09 (1H, m, Py), 7.61, 7.60 (2H, d, Ph), 7.50 (1H, s, Py), 7.16, 7.14 (1H, d, Ph), 2.46 (3H, s, CH_3), 1.55 (3H, s, MTO–CH_3); ^{13}C NMR (d^6-DMSO, 100 MHz, r.t.): δ (ppm) = 150.42, 149.64, 149.51, 139.04, 138.77, 133.65, 125.95, 125.83, 123.73, 122.60, 122.49, 116.00, 25.90, 21.80; MS (CI): m/z = 460.8 $[M]^+$, 447.8 $[M - CH_3]^+$,446.9 $[M - O]^+$, 210.1 $[M - MTO]^+$, 250.0 $[MTO]^+$.

Compound **3**: yellow powder, Yield: 74%. $C_{13}H_{11}ClN_3O_3Re$ (479), elemental analysis: Theory (C: 32.60; H: 2.32; N: 8.77), Found (C: 32.62; H: 2.33; N: 8.70); IR (KBr, ν cm^{-1}): 3068, 1602, 1589, 1491, 1442, 950, 925, 752; ^1H NMR (d^6-DMSO, 400 MHz, r.t.): δ (ppm) = 13.44 (1H, s, NH), 8.77, 8.76 (1H, d, Py), 8.36, 8.33 (1H, d, Py), 8.07, 8.06, 8.03 (1H, t, Py), 7.68 (2H, s, Ph), 7.58, 7.57 7.56 (1H, t, Py), 7.29, 7.27 (1H, d, Ph), 1.78 (3H, s, MTO–CH_3); ^{13}C NMR (d^6-DMSO, 100 MHz, r.t.): δ (ppm) = 152.22, 149.84, 147.98, 138.36, 127.54, 125.71, 123.54, 122.28, 26.68; MS (CI): m/z = 462.7 $[M - CH_3]^+$, 229.9 $[M - MTO]^+$.

Compound **4**: orange powder, Yield: 81%. $C_{12}H_{11}N_4O_3Re$ (446), elemental analysis: Theory (C: 32.36; H: 2.49; N: 12.58), Found (C: 33.05; H: 2.56; N: 12.63); IR (KBr, ν cm^{-1}): 3079, 1589, 1481, 1454, 952, 927, 784; ^1H NMR (d^6-DMSO, 400 MHz, r.t.): δ (ppm) = 13.75

(1H, s, NH), 8.78, 8.77 (1H, d, Py), 8.39, 8.37 (2H, d, Py), 8.07, 8.06, 8.03 (2H, t, Py), 7.57–7.60 (1H, m, Py), 7.27–7.30 (1H, m, Py), 1.87 (3H, s, MTO–CH3); ^{13}C NMR (d^6-DMSO, 100 MHz, r.t.): δ (ppm) = 152.73, 149.92, 148.28, 144.87, 138.29, 126.87, 122.53, 119.02, 26.62; MS (CI): m/z = 432.7 $[M - CH_3]^+$, 234.8 $[ReO_3]^+$, 196.8 $[M - MTO]^+$.

Compound **5**: yellow powder, Yield: 80%. $C_{17}H_{14}N_3O_3Re$ (495), elemental analysis: Theory (C: 41.29; H: 2.85; N: 8.50), Found (C: 41.11; H: 2.84; N: 8.49); IR (KBr, ν cm^{-1}): 3072, 1597, 1475, 1461, 958, 929, 761; ^{1}H NMR (d^6-DMSO, 400 MHz, r.t.): δ (ppm) = 13.19 (1H, s, NH), 8.57, 8.56 (1H, d, Py), 8.50, 8.48 (1H, d, Ph), 8.19, 8.16 (1H, d, Ph), 8.09, 8.07 (1H, d, Ph), 7.90, 7.88, 7.86 (1H, t, Ph), 7.78, 7.76 (1H, d, Ph), 7.71, 7.69, 7.67 (1H, t, Ph), 7.64, 7.62 (1H, d, Py), 7.24–7.32 (2H, m, Ph), 1.90 (3H, s, MTO–CH_3); ^{13}C NMR (d^6-DMSO, 100 MHz, r.t.): δ (ppm) = 151.09, 149.03, 147.65, 137.90, 130.95, 129.21, 128.70, 128.55, 127.80, 123.37, 119.67, 25.42; MS (CI): m/z = 250.6 $[MTO]^+$, 245.8 $[M - MTO]^+$.

Compound **6**: yellow powder, Yield: 84%. $C_{18}H_{16}N_3O_3Re$ (509), elemental analysis: Theory (C: 42.51; H: 3.17; N: 8.26), Found (C: 42.18; H: 3.35; N: 7.53); IR (KBr, ν cm^{-1}): 3063, 1603, 1594, 1511, 1480, 1428, 955, 929, 748; ^{1}H NMR (d^6-DMSO, 400 MHz, r.t.): δ (ppm) = 13.06 (1H, s, NH), 8.55, 8.53 (1H, d, Py), 8.17, 8.15 (1H, d, Ph), 8.08, 8.06 (1H, d, Py), 7.89, 8.87, 7.85 (1H, t, Ph), 7.70, 7.68, 7.66 (1H, t, Ph), 7.69 (1H, s, Ph), 7.47 (1H, s, Ph), 7.11, 7.09 (1H, d, Ph), 2.46 (3H, s, CH_3) 1.91 (3H, s, MTO–CH_3); ^{13}C NMR (d^6-DMSO, 100 MHz, r.t.): δ (ppm) = 150.71, 149.03, 147.55, 137.84, 132.90, 130.93, 129.16, 128.69, 128.50, 127.73, 124.97, 119.63, 25.43, 21.86; MS (CI): m/z = 509.5 $[M]^+$, 258.9 $[M - MTO]^+$, 250.9 $[MTO]^+$, 234.9 $[ReO_3]^+$.

Compound **7**: orange powder, Yield: 71%. $C_{17}H_{13}ClN_3O_3Re$ (529), elemental analysis: Theory (C: 38.60; H: 2.48; N: 7.94), Found (C: 39.20; H: 3.30; N: 6.71); IR (KBr, ν cm^{-1}): 3062, 1593, 1506, 1471, 1428, 955, 925, 756; ^{1}H NMR (d^6-DMSO, 400 MHz, r.t.): δ (ppm) = 13.37 (1H, s, NH), 8.57, 8.54 (1H, d, Py), 8.19, 8.17 (1H, d, Ph), 8.09, 8.07 (1H, d, Py), 7.90, 8.88, 7.86 (1H, t, Ph), 7.67–7.72 (3H, m, Ph), 7.27–7.31 (1H, m, Ph), 1.91 (3H, s, MTO–CH_3); ^{13}C NMR (d^6-DMSO, 100 MHz, r.t.): δ (ppm) = 152.43, 151.07, 148.98, 147.66, 138.03, 137.90, 131.03, 130.96, 129.21, 128.70, 128.64, 128.56, 127.96, 127.81, 123.40, 119.67, 25.42; MS (CI): m/z = 529.7 $[M]^+$, 279.8 $[M - MTO]^+$, 250.8 $[MTO]^+$.

4.4. Catalytic reactions

All catalytic reactions were carried out under continuous stirring in a glass flask in a water bath at room temperature. General procedure: 2 mmol of substrate, 1.2 mL of CH_2Cl_2 and 0.04 mmol of the catalyst were mixed in a flask. The reaction started when aqueous H_2O_2 (35%, 4 mmol, 0.35 mL) was added. The course of the reaction was monitored by quantitative GC analysis. Samples were taken at regular time intervals, diluted with *n*-hexane, then treated with a catalytic amount of $MgSO_4$ and MnO_2 to remove water and to destroy the excess of peroxide. The resulting slurry was filtered and the filtrate injected into a GC column. The conversion of cyclooctene and the formation of the according oxide were calculated from calibration curves ($r^2 > 0.999$) recorded prior to the reaction course.

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References

[1] R.E. Parker, N.S. Isaacs, Chem. Rev. 59 (1959) 737–799.
[2] N. Gharah, S. Chakraborty, A.K. Mukherjee, R. Bhattacharyya, Chem. Commun. (2004) 2630–2632.
[3] M. Herbert, E. Álvarez, D.J. Cole-Hamilton, F. Montilla, A. Galindo, Chem. Commun. 546 (2010) 5933–5935.
[4] C.J. Thibodeaux, W.C. Chang, H.W. Liu, Chem. Rev. 112 (2012) 1681–1709.
[5] N. Grover, F.E. Kühn, Curr. Org. Chem. 16 (2012) 16–32.
[6] M. Wu, C. Miao, S. Wang, X. Hu, C. Xia, F.E. Kühn, W. Sun, Adv. Synth. Catal. 353 (2011) 3014–3022.
[7] D. Betz, P. Altmann, M. Cokoja, W.A. Herrmann, F.E. Kühn, Coord. Chem. Rev. 255 (2011) 1518–1540.
[8] D. Betz, A. Raith, M. Cokoja, F.E. Kühn, ChemSusChem 3 (2010) 559–562.
[9] K.R. Jain, F.E. Kühn, Dalton Trans. (2008) 2221–2227.
[10] F.E. Kühn, A.M. Santos, M. Abrantes, Chem. Rev. 106 (2006) 2455–2475.
[11] Q.H. Xia, H.Q. Ge, C.P. Ye, Z.M. Liu, K.X. Su, Chem. Rev. 105 (2005) 1603–1662.
[12] W.A. Herrmann, F.E. Kühn, Acc. Chem. Res. 30 (1997) 169–180.
[13] C.C. Romão, F.E. Kühn, W.A. Herrmann, Chem. Rev. 97 (1997) 3197–3246.
[14] K.R. Jain, F.E. Kühn, J. Organomet. Chem. 692 (2007) 5532–5540.
[15] F.E. Kühn, A. Scherbaum, W.A. Herrmann, J. Organomet. Chem. 689 (2004) 4149–4164.
[16] 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) 7301–7303.
[17] E. Tosh, H.K.M. Mitterpleininger, A.M.J. Rost, D. Veljanovski, W.A. Herrmann, F.E. Kühn, Green Chem. 12 (2007) 1296–1298.
[18] W.A. Herrmann, A.M.J. Rost, E. Tosh, H. Riepl, F.E. Kühn, Green Chem. 10 (2008) 442–446.
[19] M. Carril, P. Altmann, M. Drees, W. Bonrath, T. Netscher, J. Schütz, F.E. Kühn, J. Catal. 283 (2011) 55–67.
[20] M. Carril, P. Altmann, W. Bonrath, T. Netscher, J. Schütz, F.E. Kühn, Catal. Sci. Technol. 2 (2012) 722–724.
[21] W.A. Herrmann, F.E. Kühn, C.C. Romão, H. Tran Huy, M. Wang, R.W. Fischer, P. Kiprof, W. Scherer, Chem. Ber. 126 (1993) 45–50.
[22] F.E. Kühn, J. Mink, W.A. Herrmann, Chem. Ber. 130 (1997) 295–298.
[23] W.A. Herrmann, F.E. Kühn, M.R. Mattner, G.R.J. Artus, M.R. Geisberger, J.D.G. Correia, J. Organomet. Chem. 538 (1997) 203–209.
[24] J. Rudolph, K.L. Reddy, J.P. Chiang, K.B. Sharpless, J. Am. Chem. Soc. 119 (1997) 6189–6190.
[25] C. Copéret, H. Adolfsson, K.B. Sharpless, Chem. Commun. 16 (1997) 1565–1566.
[26] C. Copéret, H. Adolfsson, T.A.V. Khuong, A.K. Yudin, K.B. Sharpless, J. Org. Chem. 63 (1998) 1740–1741.
[27] H. Adolfsson, A. Converso, K.B. Sharpless, Tetrahedron Lett. 40 (1999) 3991–3994.
[28] 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) 3603–3615.
[29] P. Ferreira, W.M. Xue, É. Bencze, E. Herdtweck, F.E. Kühn, Inorg. Chem. 40 (2001) 5834–5841.
[30] M.D. Zhou, K.R. Jain, A. Günyar, P.N.W. Baxter, E. Herdtweck, F.E. Kühn, Eur. J. Inorg. Chem. (2009) 2907–2914.
[31] S.A. Hauser, V. Korinth, E. Herdtweck, M. Cokoja, W.A. Herrmann, F.E. Kühn, Eur. J. Inorg. Chem. (2010) 4083–4090.
[32] K. Kiersch, Y. Li, K. Junge, N. Szesni, R.W. Fischer, F.E. Kühn, M. Beller, Eur. J. Inorg. Chem. (2012) in press.
[33] W.A. Herrmann, J.D.G. Correia, M.U. Rauch, G.R.J. Artus, F.E. Kühn, J. Mol. Catal. 118 (1997) 33–45.
[34] M. Zhou, J. Zhao, J. Li, S. Yue, C. Bao, J. Mink, S. Zang, F.E. Kühn, Chem. Eur. J. 13 (2007) 158–166.
[35] M.D. Zhou, S.L. Zang, E. Herdtweck, F.E. Kühn, J. Organomet. Chem. 693 (2008) 2473–2477.
[36] A. Capapé, M.D. Zhou, S.L. Zang, F.E. Kühn, J. Organomet. Chem. 693 (2008) 3240–3244.
[37] M.D. Zhou, Y. Yu, A. Capapé, K.R. Jain, E. Herdtweck, X.R. Li, J. Li, S.L. Zhang, F.E. Kühn, Chem. Asian J. 4 (2009) 411–418.
[38] Z. Xu, M.D. Zhou, M. Drees, H. Chaffey-Millar, E. Herdtweck, W.A. Herrmann, F.E. Kühn, Inorg. Chem. 48 (2009) 6812–6822.
[39] P. Altmann, M. Cokoja, F.E. Kühn, J. Organomet. Chem. 701 (2012) 51–55.
[40] J. Reedijk (Chapter 13.2), Comprehensive Coordination Chemistry, vol. 2, Pergamon, Oxford, 1987.
[41] E. Quiroz-Castro, S. Bernès, N. Barba-Behrens, R. Tapia-Benavides, R. Contreras, H. Nöth, Polyhedron 19 (2000) 1479–1484.
[42] S. Wang, S. Yu, Q. Luo, Q. Wang, J. Shi, Q. Wu, Transit. Met. Chem. 19 (1994) 205–208.
[43] J. Mink, G. Keresztury, A. Stirling, W.A. Herrmann, Spectrochim. Acta Part A 50 (1994) 2039–2057.
[44] L.K. Thompson, B.S. Ramaswamy, E.A. Seymour, Can. J. Chem. 55 (1977) 878–888.
[45] T.J. Lane, I. Nakagawa, J.L. Walter, A.J. Kandathil, Inorg. Chem. 1 (1962) 267–276.
[46] M. Ichikawa, S. Nabeya, K. Muraoka, T. Hisano, Chem. Pharm. Bull. 27 (1979) 1255–1264.
[47] J.R. Sams, T.B. Tsin, J. Chem. Soc. Dalton Trans. (1976) 488–496.
[48] T.A. Kabanos, A.D. Keramidas, D. Mentzafos, U. Russo, A. Terzis, J.M. Tsangaris, J. Chem. Soc. Dalton Trans. (1992) 2729–2733.
[49] A. Tavman, B. Ülküseven, S. Birteksöz, G. Ötük, Folia Microbiol. 48 (2003) 479–483.
[50] S.M. Nabavizadeh, A. Akbari, M. Rashidi, Dalton Trans. (2005) 2423–2427.
[51] A.E. Ceniceros-Gómez, N. Barba-Behrens, S. Bernès, H. Nöth, S.E. Castillo-Blum, Inorg. Chem. Acta 304 (2000) 230–236.
[52] M.S. Saraiva, S. Quintal, F.C.M. Portugal, T.A. Lopes, V. Félix, J.M.F. Nogueira, M. Meireles, M.G.B. Drew, M.J. Calhorda, J. Organomet. Chem. 693 (2008) 3411–3418.
[53] Y. Gao, Y. Zhang, C. Qiu, J. Zhao, Appl. Organometal. Chem. 25 (2011) 54–60.
[54] C.J. Qiu, Y.C. Zhang, Y. Gao, J.Q. Zhao, J. Organomet. Chem. 694 (2009) 3418–3424.
[55] R. Schiffmann, A. Neugebauer, C.D. Klein, J. Med. Chem. 49 (2006) 511–522.