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Bidentate Lewis Base Adducts of Methyltrioxidorhenium(VII): Ligand Influence on Catalytic Performance and Stability

Ming-Dong Zhou,[a] Kavita R. Jain,[a] Alev Günyar,[a] Paul N. W. Baxter,[b] Eberhardt Herdtweck,[a] and Fritz E. Kühn*[a]

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Methyltrioxidorhenium (MTO) forms 1:1 adducts of the general formula $CH_3ReO_3{\cdot}L_2$ with bidentate Lewis bases (L_2 = 5,5′-dimethyl-2,2′-bipyridine, 5,5′-diamino-2,2′-bipyridine, 4,4′-dibromo-2,2′-bipyridine, 5,5′-dibromo-2,2′-bipyridine, diethyl 2,2′-bipyridine-5,5′-dicarboxylate, 1,10-phenanthroline-5,6-dione, 3,6-di(2-pyridyl)pyridazine). Due to the steric demands of the ligands, the complexes display a distorted octahedral geometry as confirmed by solid state X-ray crystallography. The rhenium center is disordered in all examined crystal structures. The complexes synthesized are thermally stable but sensitive to light and moisture. The 2,2′-bipyridine derived complexes exhibit good catalytic activities for cyclooctene epoxidation in a biphasic H_2O_2/organic solvent catalytic system using hydrogen peroxide as oxidizing agent. The functional groups on the bipyridine rings play an important role with respect to the differences in formation, stability and activity of the complexes. Their influence depends largely on their electron donor capabilities.

Introduction

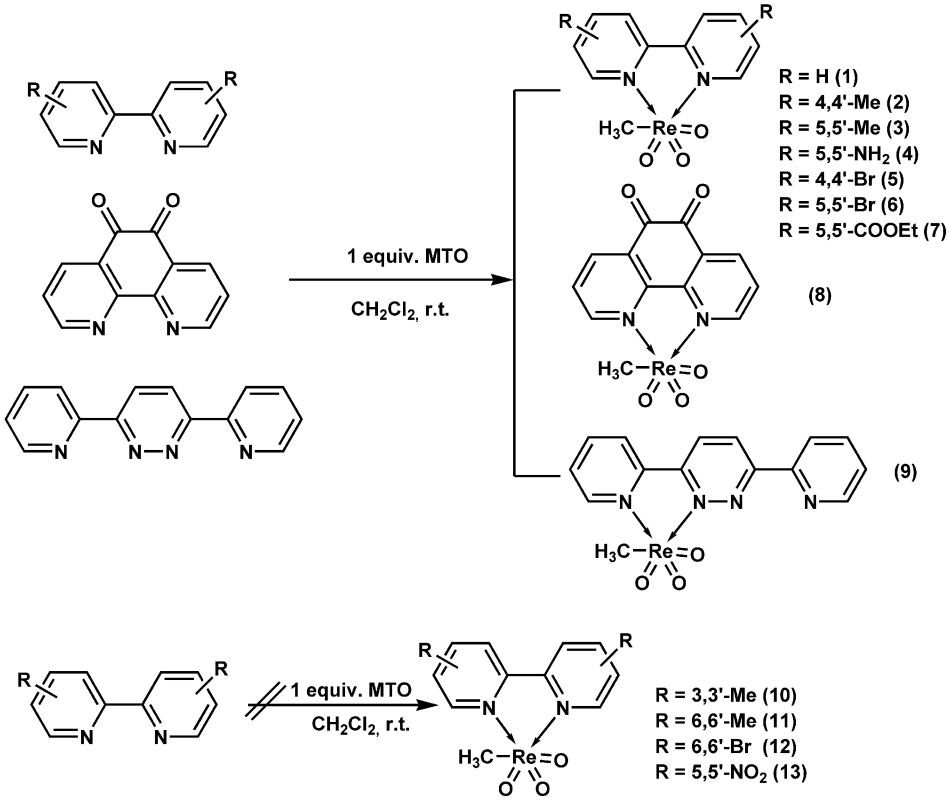
Methyltrioxidorhenium (MTO), nowadays used both as an extremely versatile catalyst and a catalyst precursor for a broad variety of organic reactions, was first described in 1979.[1] A breakthrough with respect to applications came only about ten years after the first synthesis of MTO when a more efficient synthetic route was reported by Herrmann et al.[2] Today a number of derivatives of MTO are known and easily accessible. Several of these compounds, particularly MTO itself, have found a variety of interesting applications as homogeneous or immobilized catalysts.[3] Among these numerous catalytic applications, olefin epoxidation is one of the most thoroughly examined.[4] MTO is commonly used, with hydrogen peroxide, as an oxidizing agent forming a biphasic (H_2O_2/organic solvent) system. The only by-product in the olefin epoxidation with H_2O_2 is water, which is environmentally acceptable, particularly when compared to usual by-products of other such reactions.[5] Another important advantage of MTO is its stability in aqueous media. It turned out, however, that the production of water combined with the pronounced Lewis-acidity of MTO has a tendency to promote ring opening reactions of sensitive epoxidation products by formation of diols.[6] The presence of Lewis bases suppresses the likelihood of such epoxide ring opening. It was found that the use of aromatic N-donor ligands as additives together with MTO leads to higher activities and selectivities in epoxidation catalysis rather than MTO alone.[7,8] Consequently, a variety of N-base adducts of MTO have been isolated, characterized and applied for the epoxidation of olefins as catalysts.[9,10] A literature survey shows that, among the plethora of these adducts, just a few of the bidentate donor adducts of MTO have been isolated and fully characterized with respect to their synthesis and application as epoxidation catalysts,[10b,11] in contrast to the far more extensive studies of many monodentate MTO Lewis base complexes.

In this paper a variety of bidentate Lewis base-MTO adducts is selected to investigate ring substitution effects on the adduct formation, stability, catalytic activity and the spectroscopic data of the respective compounds.

Results and Discussion

In a previous work,[10b] the synthesis of some MTO bipyridine derived complexes has been described. Among the complexes mentioned therein are methyl(2,2′-bipyridine)-trioxidorhenium and methyl(4,4′-dimethyl-2,2′-bipyridine)-trioxidorhenium, which are also included in this paper as complexes **1** and **2** in order to facilitate further discussion. Scheme 1 shows the reactions of MTO with various bidentate Lewis bases. Among them, however, only the complexes **1**–**9** could be isolated and characterized. It was observed that the coordination of Lewis bases with MTO is strongly

[a] Molecular Catalysis, Catalysis Research Center, Technische Universität München,
Lichtenbergstrasse 4, 85747 Garching bei München, Germany
Fax: +49-(0)89-289-13473
E-mail: fritz.kuehn@ch.tum.de
[b] Institut Charles Sadron, Université Louis Pasteur,
23 rue du Loess BP 20, 67083 Strasbourg, France
Fax: +33-(0)-388-41-4099
E-mail: baxter@ics.u-strasbg.fr



Scheme 1. Synthesis of complexes **1**–**9** and hypothetical formulae of complexes **10**–**13**.

affected both by steric and electronic effects as a result of the substituents on the pyridine ring moieties of the Lewis bases.

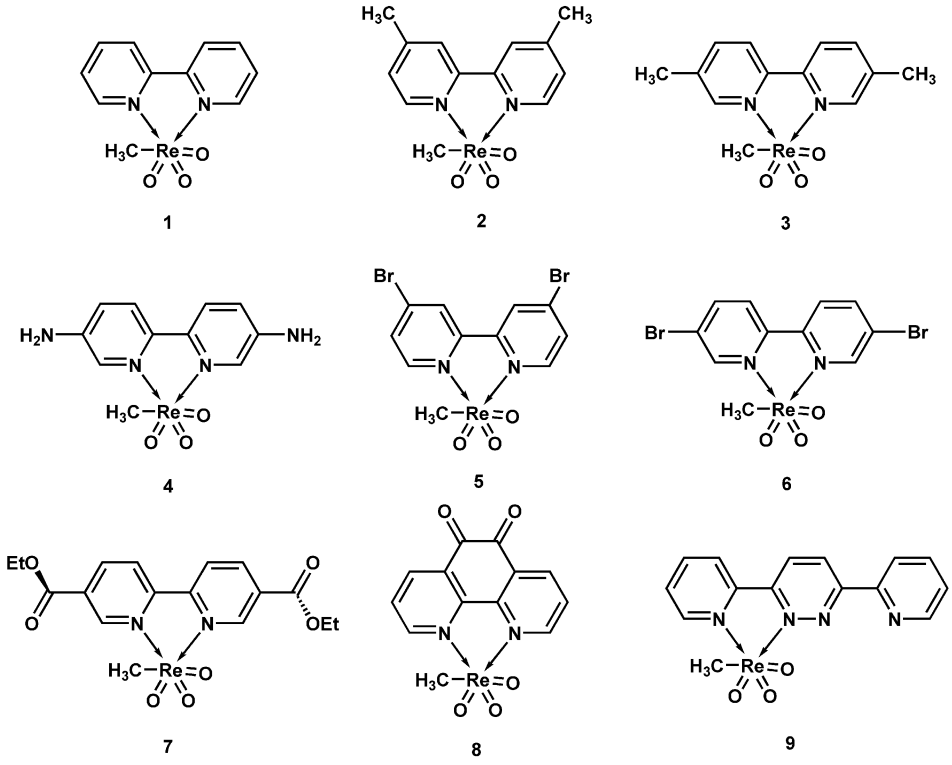
Synthesis and Spectroscopic Characterization of Complexes 1–9

Scheme 2 exhibits the complexes **1**–**9**, which were synthesized via reaction of MTO with bidentate Lewis bases in dichloromethane solution. The reaction was carried out at room temperature and isolated yields higher than 75% were obtained. In contrast to some of the monodentate Lewis base adducts of MTO, all synthesized bidentate complexes with the exception of complex **4** were found to be stable at room temperature – both in the solid state and in solution, when kept under argon. The solids, however, are sensitive to light and moisture, eventually decomposing into black residues. Complexes **1**–**3** and **5**–**9** are soluble in some polar organic solvents such as CH_3CN, CH_2Cl_2, $CHCl_3$ and THF while complex **4** is moderately soluble only in DMSO. The characteristic data of complexes **1** and **2** are included in Table 1 for comparison.[10b]

The IR spectra of the complexes **1**–**9** show a strong or very strong symmetric Re=O stretching vibration in the region of 935–946 cm^{-1} whilst the asymmetric Re=O stretching vibration lies between 905–918 cm^{-1} (see Table 1). Compared to the vibrations of non-coordinated MTO, the Re=O bands of complexes **1**–**9** are significantly red-shifted due to the donor capacity of the respective ligands in the solid state. However, the ν(Re=O) bands of complexes **1**–**9** are too close (within the error range) to allow a profound discussion with respect to the influence of the different ligands. This unfortunate fact has been already recognized in the literature.[10b]

The corresponding force constants of the Re=O bonds are calculated based on the ν (Re=O) values (see Table 1). The force constants of complexes **1**–**9** range from 7.32 to 7.49 m dyn $Å^{-1}$ and are considerably lower than that of MTO (8.31 m dyn $Å^{-1}$), reflecting the influence of the additional electron density donated from the Lewis base ligand to the rhenium center. However, when compared to the force constants of $CpReO_3$ (7.08 m dyn $Å^{-1}$) and Cp^*ReO_3 (6.95 m dyn $Å^{-1}$),[6a,12] the values obtained for the complexes described in this work are comparatively higher indicating stronger Re=O bonds in the case of the MTO Lewis base adducts. This is also in accord with the experimental results that complexes **1**–**9** show better stability at room temperature than $CpReO_3$.[6a,12]

^1H NMR spectra of complexes **1**–**9** were measured at room temperature using $CDCl_3$ as solvent (complex **4** was measured in [D_6]DMSO because of its poor solubility in $CDCl_3$). Complex **3** was also studied in DMSO for comparison to complex **4**. The ^1H NMR spectroscopic data of the Re–CH_3 group (Table 1) again clearly reflect the electron-donating capacity of the ligands. The stronger the donor ability of the Lewis base, the larger, in general, are the observed chemical shift differences in the ^1H NMR to that of non-coordinated MTO. As shown in Table 1, the chemi-



Scheme 2. Structures of Complexes **1**–**9**.

Table 1. Selected IR (KBr), ^{1}H NMR spectroscopic data and calculated force constants *f*(Re=O) for MTO and compounds **1**–**9**.

	ν(Re=O) [cm^{-1}]			*f*(Re=O)	δ_{Re-CH3}	Deuterated
	ν_s	ν_{as}	$\nu_{average}$	mdyn Å^{-1}	ppm	solvent
MTO	999 s	957 vs	978	8.25[a]	2.67	$CDCl_3$
					1.91	[D$_6$]DMSO
1	935 s	908 vs	921.5	7.32[a]	1.63	$CDCl_3$
2	938 s	913 vs	925.5	7.37[a]	1.20	$CDCl_3$
3	940 s	912 vs	926	7.39	1.08	$CDCl_3$
					0.89	[D$_6$]DMSO
4	938 s	905 vs	921.5	7.32	0.55	[D$_6$]DMSO
5	937 s	913 vs	925	7.37	2.60	$CDCl_3$
6	946 vs	918 vs	932	7.49	2.61	$CDCl_3$
7	941 vs	914 s	927.5	7.42	2.56	$CDCl_3$
8	944 vs	917 s	930.5	7.46	2.59	$CDCl_3$
9	946 s	918 vs	932	7.49	2.49	$CDCl_3$

[a] The minor error of the force constant calculations in reference[10b] have been corrected here.

cal shifts of Re–CH_3 protons of free MTO are located at δ = 2.67 ppm in $CDCl_3$ and 1.91 ppm in DMSO, the latter being most likely due to a DMSO adduct. In the case of complex **1** (having no substituents on the Lewis base ligand) the Re–CH_3 protons shift are observed at δ = 1.63 ppm in $CDCl_3$. Complexes **2** and **3**, bearing 4,4′- and 5,5′-methyl groups, show the proton signal of the Re–CH_3 group at δ = 1.20 ppm (**2**) and 1.08 ppm(**3**). Complex **4**, bearing the strong donor group NH_2 on the ligand, exhibits a stronger high field shift [$\Delta(\delta)$ = 1.36 ppm] in DMSO than complex **3** [$\Delta(\delta)$ = 1.02 ppm] under the same conditions. The ligands of either of the complexes are not replaced by the potentially coordinating solvent DMSO, demonstrating the comparatively strong interaction of the Re atom with the Lewis base. The chemical shift differences of the Re–CH_3 moieties between the complexes and free MTO are in the order **4**>**3**>**2**>**1**>**9**>**7**>**8**>**5**>**6**. This row is, in general, also in accord with the electron-donating capacity of the ligands in each complex. In the case of complex **9** with four nitrogen atoms, elemental analysis indicates a 1:1 coordination. It is assumed that the rhenium atom of MTO coordinates as shown in Scheme 2. Nevertheless in the room temperature NMR spectrum, only 5 groups of proton peaks (with small splits) can be observed. These represent the pyridazine protons and the H3,3′, H4,4′, H5,5′, H6,6′ protons of the pyridines. In order to clarify the coordination mode between the Re atom of MTO and the N atoms of the ligand, a temperature-dependent ^{1}H NMR experiment was also performed in CD_2Cl_2. The spectrum shows that the original 5 peak groups split into 10 groups when the temperature is lowered to –90 °C (see Figure 1). This result is in accordance with the expected coordination of the Re to the ligand, and with the assumption of a rapid exchange of the MTO moiety between the two bidentate ligand sites at higher temperatures.

The CI/FAB mass spectra show the molecular ionic peaks of complexes **3** and **4**. For complex **4**, a $[M - 16]^+$ peak indicating a loss of oxygen atom of MTO can be seen. In the case of complexes **5**–**7**, a $[M - CH_3]^+$ peak indicates the loss of the MTO methyl group. However, the spectra of complexes **8** and **9** show the mass peaks of the ligands and MTO separately.

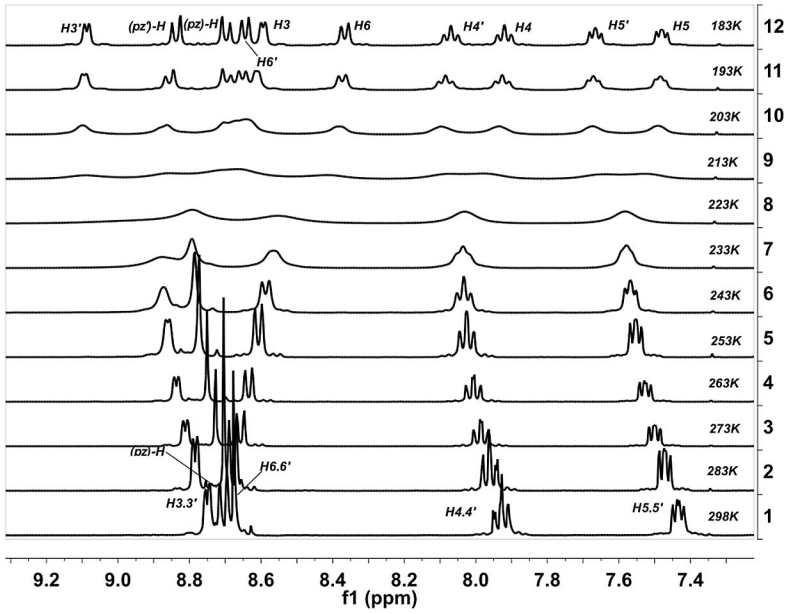


Figure 1. Temperature-dependent ^{1}H NMR spectra of complex **9**.

Steric and Electronic Effects in the Coordination of Lewis Bases to MTO

Extensive experimental work was conducted in order to obtain more information about the steric and electronic effects of various substituents on the different positions of the pyridine rings. Scheme 2 shows the compounds obtained for the coordination of all the examined Lewis bases with MTO.

It is straightforward to observe that both steric and electronic effects play important roles in the adduct-formation process. In the case of the 3,3′-, 4,4′-, 5,5′- and 6,6′-disubstituted bipyridines, the formation of adducts is affected greatly by the stereochemistry of the complexes. Complexes **2**–**7**, all of which bear the substituents on the 4,4′- and 5,5′-positions, could be easily isolated on mixing an equivalent amount of the corresponding ligand solution with MTO. However, the attempt to synthesize or isolate complexes **10**–**12** under similar conditions failed and resulted only in unreacted ligands present along with MTO in solution. This is attributed to the steric hindrance caused by the proximity of the ligand substituents to the metal center in the case of **11** and **12**, and in the case of **10**, the enforced twisting of the bipyridine rings from the planar geometry favoured for optimal coordination (to the best of our knowledge, 3,3′-dibromo-2,2′-bipyridine is unknown). This indicates that the substituents in the 6,6′-position of 2,2′-bipyridine or in the 2,9-position of 1,10-phenanthroline are too sterically demanding to allow coordination to MTO. The formation constants of MTO and different CH_3 disubstituted 2,2′-bipyiridines have been studied based on results obtained via UV/Vis spectroscopy. In dichloromethane solution, the formation constants of complexes **2** (4,4′-substitution) and **3** (5,5′-substitution) are $(3.9 \pm 0.2)\times10^3$ and $(1.3 \pm 0.1)\times10^3$, respectively. Nevertheless, under the same conditions, the values for the un-isolable complexes **10** (3,3′-substitution) and **11** (6,6′-substitution) are only 2.9 ± 0.5 and 1.2 ± 0.3 which are too small to fit into the prerequisites of the adduct formation. These results strongly support our assumptions described above. A detailed formation constant calculation about MTO and MoO_2Cl_2 Lewis base adducts has been published previously.[13]

By using different substituents in the 4,4′- and 5,5′-positions which present no steric interference, the electronic effect is seen to be a dominant factor in the coordination of Lewis bases to MTO. In this work, varied substituents on the 5,5′-position including NH_2, CH_3, Br, COOEt and NO_2 have been investigated. The donor abilities of these substituted groups are in the order NH_2>CH_3>COOEt>Br>NO_2. Nevertheless, all bipyridine ligands with these substituents form complexes with MTO with the exception of the 5,5′-NO_2 substituent. It is found that when employing electron-withdrawing groups, as long as the Lewis basicity of bipyridine is not significantly decreased by these substituents – the adducts are formed (as seen in the cases of **5** and **6**). However, the synthesis of the hypothetical complex **13** was unsucessful (affording only free ligand and free MTO) as the donor ability of the ligand is strongly reduced by the nitro groups. Considering the stability of the complexes, however, the strongest donor ligand leads to the least stable product. In the case of complex **4**, the solid is far less stable than all other examined complexes and has to be kept under argon at lower temperature. This may be due to the strong NH_2 substituted donor ligand significantly weakening the Re=O and the Re–CH_3 bonds of MTO after coordination. Accordingly, these bonds are easily broken rendering the complex unstable. The loss of an oxygen atom of MTO in the FAB/MS spectrum of **4** also supports this

assumption. However **3**, **5** and **7** are of similar stability and are all more stable than **4**, suggesting that the electronic effects of the ligands' functional groups on complex stability is limited. Complex **6** shows a relatively weaker ligand complexation as compared to **3**, **5** and **7**. It decomposes gradually into free MTO and ligand at room temperature in air after a few days.

X-ray Crystal Structure of Complex 7

The solid-state structure of complex **7** was examined and the result is shown in Figure 2. The complex displays a distorted octahedral geometry with a pyramidal *facial* arrangement of the three oxygen atoms. Two double-bonded oxygen atoms and the bidentate Lewis base ligand occupy the equatorial positions, while the methyl group and the remaining oxygen atom reside in the apical sites in the *trans* position. However, the structure of complex **7** is disordered with respect to the position of metal center, similar to the crystal structures of complexes **1** and **2** reported previously.[10b] The metal center was found either above (95% probability) or below (5% probability) the equatorial plane. Accordingly the reliability of the determination of the bond lengths and the bond angles is rather limited.

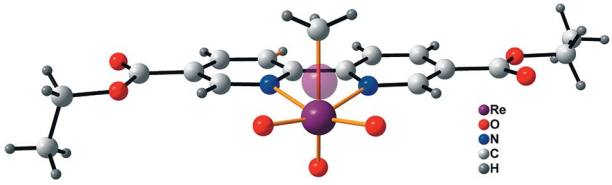


Figure 2. Ball-and-stick representation[17] of compound **7** in the solid state. The observed disorder of the rhenium atom is indicated by a translucent ball.

Applications as Epoxidation Catalysts

Complexes **3**–**9** were examined as catalysts for the epoxidation of cyclooctene using hydrogen peroxide as oxidant. The same reactions using complexes **1** and **2** as catalysts have been described previously.[10b] However for the sake of a more complete and accurate discussion, these experiments have been repeated, employing identical reaction conditions as in the cases **3**–**9**. The minor differences in the results obtained to those previously published, are attributed to the different reaction environments. Details of the catalytic reactions are given in the experimental section. Blank reactions show that there is no significant formation of epoxide in the absence of catalyst. A catalyst:oxidant:substrate ratio of 1:200:100 was used in all cases, unless stated otherwise. All catalytic reactions follow first order kinetics in which the reaction conversion increases steadily for the first two hours and then slows down.

In the reaction systems, the clear-yellow color of the solution containing the substrate and the catalysts darkens after the addition of hydrogen peroxide representing the formation of the active species, i. e. monoperoxo and diperoxo complexes.[6] In the case of complexes **1**, **8** and **9**, however, the yellow color disappears after one hour of reaction time and the color does not turn to deeper yellow again, even after addition of more H_2O_2 in the solution, reflecting the decomposition of the catalysts.

In the case of **8** and **9** (with 1,10-phenanthroline-5,6-dione and 3,6-di(2-pyridyl)pyridazine ligands), the results obtained show the highest conversion of 35% (**8**) and 65% (**9**) after 4 h and show no further changes even after 24 h due to catalyst decomposition (see Figure 3).

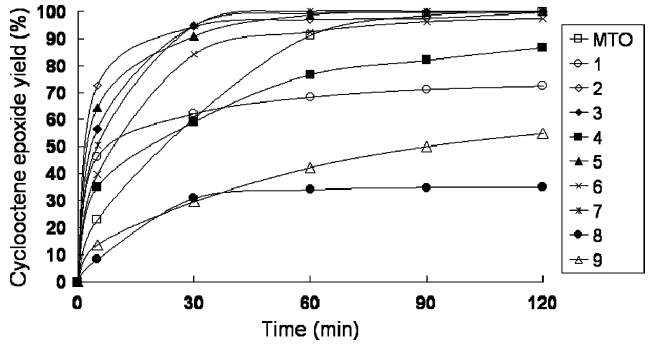


Figure 3. Time-dependent yield of cyclooctene epoxide in the presence of MTO and compounds **3**–**9** as catalysts at room temperature with 1 mol-% catalyst charge.

Most of the examined 2,2′-bipyridine-derived complexes **1**–**7** exhibit high activities on cyclooctene epoxidation. After one hour of reaction time, complexes **2**, **3**, **5** and **7** reach almost 100% epoxide yield (see Figure 3). Complex **4** and **6** are somewhat slower but also reach 87% and 90% epoxide yield after two hours. Complex **1**, owing to the catalyst decompostion, reaches 72% after two hours and shows no further changes after 4 h and 24 h. The turnover frequencies of the complexes **1**–**7** lie between 420 and 870 h^{-1} and are significantly higher than that of MTO (280 h^{-1}) under the same conditions, clearly indicating that the reactions are accelerated on application of bipyridine ligands (see Table 2 and Figure 3). Complex **2** ligated with 4,4′-dimethyl-2,2′-bipyridine shows the highest TOF (870 h^{-1}), followed by the 4,4′-substituted bromo ligand complex **5** (780 h^{-1}). The TOFs of 5,5′-dimethyl- and 5,5′-diethoxycarbonyl-substituted complexes **3** (680 h^{-1}) and **7** (605 h^{-1}) are somewhat lower than that of complexes **2** and **5**. It seems that the position of ring-substitution on the bipyridine ligand plays an important role on the catalytic activities of the complexes. Both the examined 4,4′-disubstituted complexes exhibit higher activities than the 5,5′-disubstituted complexes. However, as to be expected, the catalytic performance differences when applying different substituted groups (electron-withdrawing vs. electron-donating ones) on the bipyridine rings are not particularly pronounced. Only complex **4**, bearing the strongest donor ligand NH_2, displays a lower catalytic activity (90% epoxide yield after 2 h) than the other bipyridine derived complexes (with the exception of complex **1** which indicates catalyst decomposition during the course of reaction).

Table 2. Approximate TOF values after 5 min for MTO and compounds **3**–**9** using cyclooctene as substrate.

Compound	TOF [h^{-1}]
MTO	280
1	555
2	870
3	680
4	420
5	780
6	475
7	605
8	100
9	160

It is noteworthy that all examined complexes exhibit high selectivities (>99%) for epoxide formation. The diol product obtained by the ring-opening reaction cannot be observed even after 24 h reaction time according to the GC results. It has also been observed that the examined bidentate bipyridine complexes show higher catalytic activities than the monodentate complexes described previously.[10a] Furthermore, due to the better stability of the bidentate Lewis bases adducts (most of the monodentate complexes decompose into red or back residues within a few hours on exposure to air), the bidentate complexes form more stable catalytic systems when applied in epoxidation catalysis than monodentate complexes.[10a]

Conclusions

Several bidentate Lewis bases form readily available, stable but light-sensitive complexes with MTO. The X-ray crystal structure of these complexes display a distorted octahedral geometry. Due to the metal disorder no reliable determination of the bond lengths and the bond angles can be obtained. The coordination of bidentate Lewis base ligands to MTO is governed by both electronic and steric effects due to the contributions of different functional groups on the bipyridine ligands. The ^{1}H NMR spectra clearly reflect the electron-donating capability of the ligands. The stronger the donor ability of the Lewis base, the larger, in general, are the observed ^{1}H NMR shift differences compared to free MTO. The bipyridine derived complexes show high selectivities and, in most cases, good catalytic activities for olefin epoxidation. The best catalysts among the examined ones are those with only moderate donating capabilities and without steric hindrance of the ring substituents with respect to the MTO moiety.

Experimental Section

General: All preparations and manipulations were carried out with standard Schlenk techniques under an oxygen- and water-free nitrogen or argon atmosphere. Solvents were dried by standard procedures (*n*-hexane, THF and Et_2O over Na/benzophenone; CH_2Cl_2 over CaH_2), distilled, and kept under argon over molecular sieves (4 Å). IR spectra were recorded on a Nicolet 5700 FT-IR spectrometer using KBr pellets as the IR matrix. ^{1}H NMR spectra were measured with a Varian 270 and 400 MHz Bruker Avance DPX-400 spectrometer. Elemental analyses were performed with a Flash EA 1112 series elemental analyser. FAB and CI mass spectra (isobutene as CI gas) were obtained with a Finnigan MAT311A and a MAT90 spectrometer. Mass spectra (*m*/*z* values) are based on the isotope ^{187}Re. Catalytic runs were monitored by GC methods on a Varian CP-3800 instrument equipped with a FID and a VF-5ms column. The starting materials, namely the ligands[14] and MTO[15] were prepared according to literature known procedures. 3,6′-di(2-pyridyl)pyridazine were obtained from Aldrich and used without further purification. The synthesis of complexes **1** and **2** and their characterization data is described in the published literature.[10b]

Syntheses of Complexes: MTO (200 mg, 0.8 mmol) was dissolved in CH_2Cl_2 (10 mL) and an equally concentrated solution of ligand (0.8 mmol) in CH_2Cl_2 (10 mL) was added to the stirred solution. The yellow precipitate (**3**–**7**) was obtained immediately. After half an hour the solution was concentrated in oil pump vacuum to ca. 3 mL. The powder was obtained by filtration, washed with *n*-hexane and dried under reduced pressure.

(5,5′-Dimethyl-2,2′-bipyridine)methyltrioxidorhenium (3):[14a] Yield 319 mg, 92%. ^{1}H NMR (400 MHz, $CDCl_3$, room temp.): δ = 8.92 (s, 2 H, $H^{6,6'}$), 8.13–8.11 (d, 2 H, $H^{3,3'}$), 7.88–7.86, (d, 2 H, $H^{4,4'}$), 2.49 (s, 6 H, 2×CH_3) ppm. 1.08 (s, 3 H, Re–CH_3). IR (KBr, $\tilde{\nu}$ =): $\tilde{\nu}$ = 3550 (m), 3418 (s), 3039 (w), 2921 (w), 1637 (m), 1617 (s), 1486 (m), 1386 (w), 1151 (w), 1055 (m), 940 (s), 912 (vs), 852 (s), 839 (s) cm^{-1}. MS (FAB): *m*/*z* = 434.8 $[M]^+$, 418.8 $[M - CH_3]^+$, 402.8 $[M - 2CH_3]^+$, 185.1 $[M - MTO]^+$. $C_{13}H_{15}N_2O_3Re$ (433.48): calcd. C 36.02, H 3.49, N 6.46; found C 36.04, H 3.57, N 6.42.

(5,5′-Diamino-2,2′-bipyridine)methyltrioxidorhenium (4):[14a] Yield 296 mg, 85%. ^{1}H NMR (400 MHz, DMSO, room temp.): δ = 8.19 (s, 2 H, $H^{6,6'}$), 8.06–8.04 (d, 2 H, $H^{3,3'}$), 7.27–7.25 (d, 2 H, $H^{4,4'}$), 6.21 (s, 4 H, 2×NH_2), 0.55 (s, 3 H, Re-CH_3) ppm. IR (KBr): $\tilde{\nu}$ = 3418 (s, br), 3304 (w), 3202 (sh), 1604 (s), 1581 (s), 1493 (vs), 1160 (w), 1039 (w), 938 (s), 905 (vs), 872 (sh), 839 (s). MS (CI): *m*/*z* = 435.5 $[M]^+$, 419.0 $[M - 16]^+$,187.0 $[M - MTO]^+$. $C_{11}H_{13}N_4O_3Re$ (435.45): calcd. C 30.27, H 3.23, N 12.84; found C 30.35, H 3.12, N 12.39.

(4,4′-Dibromo-2,2′-bipyridine)methyltrioxidorhenium (5):[14b] Yield 397 mg, 88%. ^{1}H NMR (400 MHz, $CDCl_3$, room temp.): δ = 8.61 (d, 2 H, $H^{3,3'}$), 8.50–8.48 (d, 2 H, $H^{6,6'}$), 7.52–7.50 (dd, 2 H, $H^{5,5'}$), 2.60 (s, 3 H, Re-CH_3) ppm. IR (KBr): $\tilde{\nu}$ = 3421 (br), 3069 (sh), 1588 (vs), 1550 (m), 1460 (s), 1139 (w), 1091 (m), 937 (s), 913 (vs), 847 (vs), 839 (vs), 710 (s), 524 (m) cm^{-1}. MS (CI): *m*/*z* = 548.3 $[M - CH_3]^+$, 312.6 $[M - MTO]^+$, 234.8 $([ReO_3]^+$. $C_{11}H_9Br_2N_2O_3Re$ (563.22): calcd. C 23.46, H 1.61, N 4.97; found C 23.61, H 1.71, N 4.94.

(5,5′-Dibromo-2,2′-bipyridine)methyltrioxidorhenium (6):[14c] Yield 338 mg, 75%. ^{1}H NMR (400 MHz, $CDCl_3$, room temp.): δ = 8.71 (s, 2 H, $H^{6,6'}$), 8.30–8.28 (d, 2 H, $H^{3,3'}$), 7.95–7.93 (d, 2 H, $H^{4,4'}$), 2.61 (s, 3 H, Re-CH_3) ppm. IR (KBr): $\tilde{\nu}$ = 3434 (br), 3093 (sh), 3051 (w), 2963 (w), 2923 (w), 1638 (br), 1585 (m), 1457 (s), 1357 (m), 1261 (m), 1107 (s), 1087 (m), 1009 (sh), 946 (vs), 918 (vs), 844 (vs), 828 (sh), 727 (sh), 664 (w) cm^{-1}. MS (CI): *m*/*z* = 548.9 $[M - CH_3]^+$, 312.9 $[M - MTO]^+$, 234.9 $([ReO_3]^+$. $C_{11}H_9Br_2N_2O_3Re$ (563.22): calcd. C 23.46, H 1.61, N 4.97; found C 23.51, H 2.09, N 4.80.

(5,5′-Diethoxycarbonyl-2,2′-bipyridine)methyltrioxidorhenium(7):[14a] Yield 400 mg, 91%. ^{1}H NMR (400 MHz, $CDCl_3$, room temp.): δ = 9.31–9.30 (s, 2 H, $H^{6,6'}$), 8.59–8.57 (d, 2 H, $H^{3,3'}$), 8.46–8.44 (dd, 2 H, $H^{4,4'}$), 4.48–4.43 (q, 4 H, 2×CH_2), 2.56 (s, 3 H, Re-CH_3), 1.46–1.43 (t, 6 H, 2×CH_3) ppm. IR (KBr): $\tilde{\nu}$ = 3435 (w), 3084 (w),

3046 (w), 2987 (sh), 1718 (vs), 1685 (s), 1609 (m), 1584 (w), 1466 (m), 1373 (s), 1294 (vs), 1270 (s), 1144 (s), 1114 (m), 941 (vs), 914 (s), 858 (vs), 763 (s). MS (CI): m/z = 536.4 $[M - CH_3]^+$, 300.8 $[M - MTO]^+$, 250.8 $[MTO]^+$. $C_{17}H_{19}N_2O_7Re$ (549.55): calcd. C 37.15, H 3.48, N 5.10; found C 37.27, H 3.53, N 5.36.

Methyl(1,10-phenanthroline-5,6-dione)trioxidorhenium (8):[14d] Yield 287 mg, 78%. ^1H NMR (400 MHz, $CDCl_3$, room temp.): δ = 9.15–9.13 (d, 2 H, $H^{6,6'}$), 8.54–8.52 (d, 2 H, $H^{4,4'}$), 7.63–7.60 (dd, 2 H, $H^{5,5'}$), 2.59 (s, 3 H, Re-CH_3) ppm. IR (KBr): $\tilde{\nu}$ = 3418 (br), 1704 (s), 1617 (m), 1575 (s), 1482 (s), 1429 (s), 1302 (m), 1256 (m), 1132 (m), 1027 (m), 944 (vs), 917 (s), 859 (vs), 848 (s), 729 (s) cm^{-1}. MS (CI): m/z = 444.6 $[M - CH_3]^+$, 210.9 $[M - MTO]^+$, 250.8 $[MTO]^+$. $C_{13}H_9N_2O_5Re$ (459.43): calcd. C 33.99, H 1.97, N 6.10; found C 34.13, H 2.19, N 6.05.

[3,6′-Di(2-pyridyl)pyridazine]methyltrioxidorhenium (9): Yield 290 mg, 75%. ^1H NMR (400 MHz, $CDCl_3$, room temp.): δ = 8.75 (d, 2 H, $H^{3,3'}$), 8.73 (d, 2 H, (pz)-H), 8.69 (d, 2 H, $H^{6,6'}$), 7.93–7.89 (t, 2 H, $H^{4,4'}$), 7.43–7.40 (dd, 1 H, $H^{5,5'}$), 2.49 (s, 3 H, Re-CH_3) ppm. IR (KBr): $\tilde{\nu}$ = 3550 (w), 3478 (m), 3416 (m), 1637 (m), 1617 (m), 1604 (m), 1587 (w), 1422 (s), 1143 (w), 1075 (w), 946 (s), 918 (vs), 840 (s), 779 (vs) cm^{-1}. MS (FAB): m/z = 235.0 $[M - MTO]^{+2}$, 251.0 $[MTO]^+$. $C_{15}H_{13}N_4O_3Re$ (483.50): calcd. C 37.26, H 2.71, N 11.59; found C 37.00, H 2.90, N 11.22.

Single Crystal X-ray Structure Determination of Complex 7: $C_{17}H_{19}N_2O_7Re$; M_r = 549.55; crystal color and shape: yellow fragment; crystal system: monoclinic; space group: $P2_1/c$ (no. 14); a = 10.002(2), b = 16.476(3), c = 11.257(2) Å; β = 97.544(17)°, V = 1839.0(6) $Å^3$; Z = 4; μ(Mo-K_α) = 6.650 mm^{-1}; $\rho_{calcd.}$ = 1.985 $g\,cm^{-3}$. The rhenium atom was found to be disordered over two positions. Due to this fact the refinements were aborted.[16]

Catalytic Reactions: *cis*-Cyclooctene (345.4 mg, 3.14 mmol), mesitylene (429 mg, internal standard), CH_2Cl_2 (2.2 mL, solvent), and 1 mol-% of compounds **3**–**9** (31.4 μmol, catalyst) were mixed in the reaction vessel under air at room temperature. With the addition of H_2O_2 (0.7 mL, ca. 6.3 mmol, 30% aqueous solution) the reaction was started.

The course of the reaction was monitored by quantitative GC analysis. Samples were taken in regular time intervals, diluted with CH_2Cl_2, and 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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