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Multiple bonds between transition metals and main-group elements, 163 [1] Nitrogen-donor adducts of organorhenium(VII) oxides: structural and catalytic aspects

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Abstract

N-base adducts of methyltrioxorhenium(VII) (**1**), characterized by their structural and spectroscopic data, are compared with respect to the influence of the pK_b values of the *N*-bases. The crystal structure of one of these derivatives, namely the adduct of Tröger's base ((5R,11R)-(+)-2,8-dimethyl-6H,12H-5,11-methanodibenzo[b,f]-[1,5]diazocine) with compound **1** (**2a**) is reported. The cell constants are as follows: $a = 1281.6(2)$ pm, $b = 833.9(1)$ pm, $c = 1705.5(2)$ pm, $\beta = 106.09(1)°$, $V = 1751.2(4) \times 10^6$ pm^3. Derivative **2a** exhibits the longest Re(VII)–N bond distance known to date. Furthermore, **2a** is the first adduct of Tröger's base whose structure has been examined by X-ray crystallography. Epoxidation and sulfoxidation catalysis with *N*-base adducts of **1** is described, the influence of the Re–N bond strength on the catalytic processes is discussed.

Keywords: Catalysis; Olefin epoxidation; Sulfoxidation; *N*-base adducts; Methyltrioxorhenium; Tröger's base

1. Introduction

Methyltrioxorhenium (**1**) has been successfully employed as catalyst in a broad variety of processes [2–17]. In particular the highly efficient catalytic oxidation system methyltrioxorhenium/H_2O_2 was the subject of extensive studies that appeared in the literature during the last few years [4]. Addition of nitrogen bases to solutions of methyltrioxorhenium (e.g. quinuclidine, 2,2′-bipyridine) enhances the selectivity towards the desired epoxides and suppresses the formation of diols [6]. A variety of Lewis base adducts of **1** has been described, but only very few structures are known and systematic investigations which also consider the catalytic activity of these compounds have not been undertaken [16]. Therefore we were tempted to examine the structural and spectroscopic properties of some *N*-donor adducts of **1** with respect to the catalytic applications of these compounds.

2. Results and discussion

2.1. Synthesis, structures and spectroscopic data of N-base adducts of methyltrioxorhenium(VII)

As soon as **1** was available by a convenient synthetic procedure [17,18] it was found that this compound is a very strong Lewis acid. This behavior leads to the formation of adducts with electron donors such as *N*-bases [19–23], O-bases [24,25], *N*-oxides [24,25], carbenes [26], and other Lewis bases [19,27]. Complex **1** is unstable in the presence of OH^- ions, decomposing under formation of ReO_4^- [28] and CH_4. Addition of *N*-bases to **1** at low temperatures in Et_2O leads to the formation of pale yellow precipitates, consisting of the *N*-base adducts of **1** (**2**) according to Eq. (1). In all examined cases this precipitate is more temperature

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[1] Communication 162 of this series, see Ref. [1].

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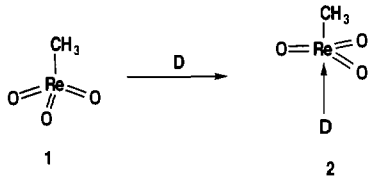
sensitive than pure **1**. Usually only one Lewis base molecule coordinates to **1**, with the one exception of NH_3, which forms an adduct of composition $CH_3ReO_3 \cdot (NH_3)_2$ [19–23].



1 2 (1)

Reaction of **1** with Tröger's base ((5R,11R)-(+)-2,8-dimethyl-6H,12H-5,11-methanodibenzo[b,f]-[1,5]diazocine) (**3**) yields nearly quantitatively complex **2a**. It is the first known chiral base adduct of **1** and also noteworthy as the first metal complex of Tröger's base [29]. It is a stable, yellow powder which can easily be crystallized. Derivative **2a** is also the first complex containing Tröger's base as ligand that has ever been examined by X-ray crystallography. The atomic coordinates are given in Table 1, crystallographic data in Table 2, and a PLATON representation of complex **2a** is shown in Fig. 1. While the Re=O and Re–C bond distances of this complex are not unusual (see Fig. 1 and Table 3), the Re–N distance is exceptional. It is the longest Re(VII)–N bond distance known to date. All reported Re(VII)–N distances in monomeric trigonal bipyramidal Lewis base adducts of organorhenium oxides range between 239 and 247 pm, more than 12 pm shorter than in the case of **2a** [19–23]. The bond distances in intramolecular Lewis base adducts are in the range between 230 and 240 pm [19–25]. Usual Re(VII)–*N*-donor bonds are around 225 pm, Re(VII)–N single bonds ca. 200 pm [20]. Obviously **2a** shows an extreme case of a very weak Re(VII)–N interaction. A comparison of selected bond distances of **2a** and other structurally known *N*-base adducts is given in Table 3. The long Re–N bond distance is very likely due to the steric bulk of Tröger's base. Despite the large Re–N distance the C–Re–O angles are in the range (97.4(3)°–

Table 1
Final coordinates and equivalent isotropic thermal parameters for **2a**

Atom	x/a	y/b	z/c	U_{eq} [Å^2]
Re(1)	0.22535(2)	0.11625(3)	0.10803(2)	0.0245
O(1)	0.3610(4)	0.1104(7)	0.1294(3)	0.0517
O(2)	0.1610(4)	0.2830(7)	0.0636(3)	0.0556
O(3)	0.1551(5)	−0.0548(7)	0.0873(3)	0.0638
N(1)	0.2416(4)	0.0612(6)	−0.0375(3)	0.0212
N(2)	0.2863(4)	−0.1564(6)	−0.1181(3)	0.0246
C(1)	0.2106(5)	0.1490(9)	0.2252(4)	0.0382
C(2)	0.2679(5)	−0.1116(8)	−0.0404(3)	0.0275
C(3)	0.1310(5)	0.0828(8)	−0.0947(3)	0.0265
C(4)	0.1224(4)	0.0070(8)	−0.1766(4)	0.0217
C(5)	0.0382(5)	0.0522(8)	−0.2443(4)	0.0253
C(6)	0.0326(5)	−0.0025(8)	−0.3219(4)	0.0254
C(7)	−0.0551(5)	0.0572(8)	−0.3946(4)	0.0332
C(8)	0.1125(5)	−0.1086(9)	−0.3306(4)	0.0311
C(9)	0.1942(5)	−0.1599(7)	−0.2644(4)	0.0266
C(10)	0.1998(4)	−0.1023(8)	−0.1868(3)	0.0227
C(11)	0.3920(5)	−0.0876(8)	−0.1185(4)	0.0304
C(12)	0.3945(5)	0.0913(8)	−0.1007(3)	0.0246
C(13)	0.4655(5)	0.1926(8)	−0.1254(4)	0.0275
C(14)	0.4662(5)	0.3561(9)	−0.1145(4)	0.0318
C(15)	0.5424(6)	0.464(1)	−0.1446(5)	0.0533
C(16)	0.3927(5)	0.4220(8)	−0.0766(4)	0.029
C(17)	0.3223(5)	0.3231(8)	−0.0508(4)	0.0249
C(18)	0.3213(5)	0.1614(7)	−0.0630(3)	0.0223

Table 2
Crystallographic data of **2a**

Formula	$C_{18}H_{21}N_2O_3Re$
f_w (g mol^{-1})	499.58
Crystal	yellow fragment
Crystal size (mm^3)	0.51 × 0.49 × 0.54
Space group	$P2_1/c$ (No. 14)
a (pm)	1281.6(2)
b (pm)	833.9(1)
c (pm)	1705.5(2)
β (°)	106.09(1)
V (pm^3)	1751.2 × 10^6
D_{calc} (g cm^{-3})	1.89
Z	4
Measured data	3971
Unique data, $I > 3.0\sigma(I)$	2547
Parameters	218
R [a]	0.028
R_w [b]	0.027

[a] $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$.
[b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$.

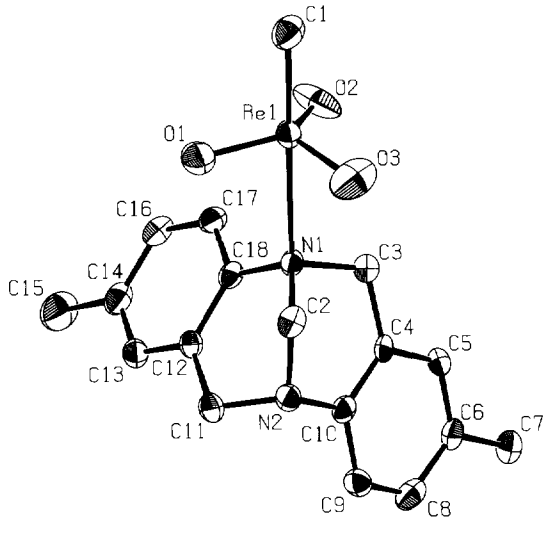


Fig. 1. PLATON representation of the (S)-enantiomer of compound **2a**. Selected bond distances [Å] and angles [deg]: Re1–O1 = 1.675(4), Re1–O2 = 1.685(5), Re1–O3 = 1.672(5), Re1–N1 = 2.589(5), Re1–C1 = 2.077(6), O2–Re1–O1 = 118.1(3), O3–Re1–O1 = 119.1(3), O3–Re1–O2 = 116.2(3), N1–Re1–O1 = 81.3(2), N1–Re1–O2 = 82.8(2), N1–Re1–O3 = 80.1(2), C1–Re1–O1 = 99.2(2), C1–Re1–O2 = 99.2(3), C1–Re1–O3 = 97.4(3), C1–Re1–N1 = 177.3(2), C2–N1–Re1 = 106.5(3), C3–N1–Re1 = 106.9(3), C3–N1–C2 = 106.2(5), C18–N1–Re1 = 115.4(3), C18–N1–C2 = 111.0(5), C18–N1–C3 = 110.4(5).

Table 3
Comparison of selected structural data of *N*-base adducts of methyltrioxorhenium (**1**)

N-base	Re–C	Re–N	O–Re–N	C–Re–N
Tröger's base	2.077(6)	2.589(5)	80.1(2)–82.8(2)	177.3(2)
^{t}butylpyridine [a]	2.085(6)	2.405(4)	83.1(2)–83.4(2)	179.7(2)
aniline [b]	2.095(5)	2.469(4)	82.3(1)–83.0(1)	179.5(2)
free **1** (MTO)	2.063(2)	—	—	—

[a] See Ref. [22].
[b] See Ref. [21].

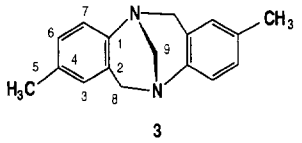
99.2(3)°) which is also observed in donor adducts of **1** with shorter Re–N bond distances (95.8(3)°–98.9(4)°). Compound **1** displays a C–Re–O angle of 105.4(1)° and 105.9(1)° respectively. These observations might indicate that the steric bulk of Tröger's base is the most important reason for the long Re–N bond distance. The weakness of the Re–N interaction in **2a** is also reflected by the Re–C bond distances of compounds **2a–2c** in comparison to **1**. In the case of **2a** this bond distance is closest to the Re–C distance in the free complex **1** (see Table 3).

The weak Re–N interaction can also be seen from the ^{17}O NMR data (recorded in $CDCl_3$). In derivative **2a** $\delta(^{17}O) = 863$ ppm, in **2b** (^{t}butylpyridine adduct of **1**) it is 882 ppm, in the quinuclidine adduct (**2d**) 906 ppm. The signal of complex **1** is observed at $\delta(^{17}O) = 829$ ppm. It is known that the chemical shift of these complexes can be regarded as an indication of the donor strength of such complexes [30]. Some solvents, e.g. THF and CH_3OH, seem to be donors of similar strength as Tröger's base, according to their chemical shifts, but THF or methanol adducts of **1** have not yet been isolated. It seems that only slightly weaker interactions between the Lewis acid **1** and Lewis bases lead to non-isolability of the resulting complexes. These assumptions are strongly supported by ^1H and ^{17}O NMR measurements. We have shown recently that in donor solvents a fast exchange equilibrium between solvent (S) and base (L) coordinated **1** exists at room temperature and above, for L = quinuclidine, aniline and S = THF [25]. An analogous equilibrium can be observed with Tröger's base and THF, indicating that both donors are of nearly equal strength. Even at −30 °C only one signal is observed.

^1H NMR spectroscopy leads to comparable results. The chemical shift of the CH_3 group of **1** is 2.61 ppm in $CDCl_3$, the CH_3 group of **2a** leads to a signal at 2.35 ppm, in **2b** at 1.80 ppm and in **2d**, the complex containing the strongest Lewis base, 1.40 ppm. In pyridine the signal of **1** is shifted to 1.67 ppm, comparable to **2b** in $CDCl_3$. The more electron density the *N*-donor ligand gives to the Lewis acidic Re(VII) center, the more high field shifted is the ^1H NMR signal of the Re–CH_3 group.

All these results are in good accord to the pK_b values [31] of the *N*-donor ligands. Quinuclidine is the strongest of the examined bases and displays a pK_b value of 3.45. For pyridine the pK_b value is 8.01, for aniline 9.36 and for Tröger's base 10.80. This comparison clearly shows the direct relationship of the pK_b values of the *N*-donor molecules to both the NMR shifts of the resulting complexes with **1** and the N–Re bond length in the adducts. However, the IR spectra of all examined adducts are quite similar ($\nu(Re{=}O)_{asym} \approx 930\,cm^{-1}$, $\nu(Re{=}O)_{sym} \approx 970\,cm^{-1}$) and a direct correlation with the pK_b values is not obvious.

The NMR signals of Tröger's base are shifted due to adduct formation, too. This is most prominently seen in the ^1H NMR signals of the protons riding on C-8 and C-9 (a numbering scheme is given below). They are shifted nearly 0.2 ppm. In the ^{13}C NMR spectrum the shift difference of C-8 and C-9 is not strongly pronounced. However, $\Delta\delta(^{13}C)$ between (not coordinated) **1** and (coordinated) **2a** is ca. 4 ppm in the case of the methyl carbon. In the case of the *N,N'*-^{t}butyl pyridine adduct of **1** (**2b**) the corresponding shift difference is nearly 6 ppm, again an indication for the stronger coordination in **2b**.



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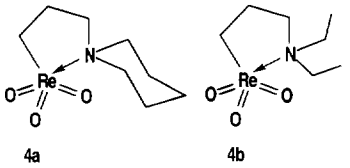
2.2. Behavior in the presence of H_2O_2

It is known that certain *N*-base complexes of methyltrioxorhenium, namely the quinuclidine adduct (**2d**), are highly selective olefin epoxidation catalysts [5,6]. It is also known that monomeric, intramolecular *N*-base adducts of organorhenium(VII) oxides are catalytically inactive [6,25]. The latter observation is probably due to the fact that certain amines can easily be oxidized to *N*-oxides in the presence of H_2O_2 and an appropriate catalyst, e.g. methyltrioxorhenium [10,11]. The resulting *N*-oxides are weaker donors than the *N*-bases and therefore less selective catalysts. In the case of intramolecular base adducts, such as compounds **4a,b**, the resulting *N*-oxides are not stable and decompose under formation of perrhenate [32].



4a 4b

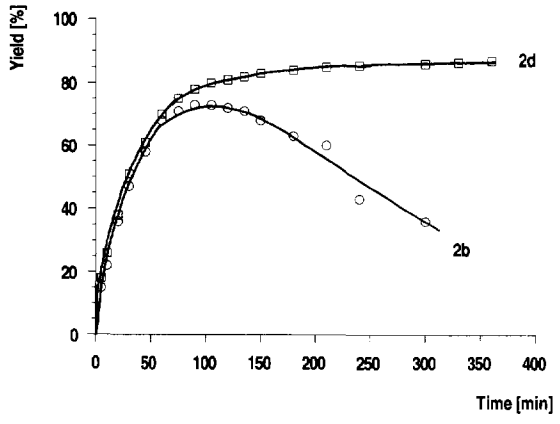


Fig. 2. Catalytic activity of $CH_3ReO \cdot$(quinuclidine) (**2d**) (6 mol%) and $CH_3ReO \cdot$(^{t}butylpyridine) (**2b**) (6 mol%) in the oxidation of cyclohexene with H_2O_2. Cyclohexene:H_2O_2:[Cat.] 1:1.5:0.01. T = 25 °C. If a ten-fold excess N-base:CH_3ReO_3 is used the resulting curve in both cases is identical with the curve for **2d** within experimental error.

Despite the fact that quinuclidine can be oxidized to the corresponding N-oxide with H_2O_2 and **1** as catalyst, **2d** is an efficient, selective and stable catalyst in olefin epoxidation. **2b** is significantly less effective. Obviously the weaker donating ligand ^{t}butylpyridine is more readily oxidized to the N-oxide which is an even weaker donor ligand than the N-base and therefore less selective and active. If a large excess ^{t}butylpyridine is added the catalytic activity of **2b** is similar to that of **2d** (Fig. 2).

Addition of chiral ligands to certain transition metal-based catalytic oxidizing systems is known to induce chirality on the obtained products [33]. As far as we are aware, the influence of chiral ligands on the selectivity of the system CH_3ReO_3/H_2O_2 is still unknown. Tröger's base ((5R,11R)-(+)-2,8-dimethyl-6H,12H-5,11-methanodibenzo[b,f]-[1,5]diazocine) seemed to be an appropriate chiral auxiliary since this ligand forms a defined adduct (**2a**) with methyltrioxorhenium as seen before. The results concerning the use of the system

Table 4
Catalytic epoxidation of olefins with the system CH_3ReO_3/H_2O_2/(+)-Tröger's base [a]

Substrate	CH_3ReO_3 [equiv.]	t [h]	H_2O_2 [equiv.]	Base [equiv.]	Conv. [b] [%]	Epoxide [b] [%]
cis-cyclooctene	0.01	3	4	0.05	50	100
	0.01	24	4	0.05	90	100
1-methylcyclo-	0.02	1	5	0.02	50	100 [c]
hexene	0.02	2	5	0.02	70	100 [c]
cyclohexene-	0.02	1	5	0.02	< 10	100 [c]
2-on						
allyl alcohol	0.013	18	4	0.08	20	100 [c]
	0.01	72	3	0.01	50	70 [c]

[a] T = 25 °C.
[b] Determined by GC-MS; error ±5%.
[c] ee = 0%.

Table 5
Catalytic oxidation of sulfides with the system CH_3ReO_3/H_2O_2/(+)-Tröger's base at different temperatures [a]

(+)-Tröger's base [equiv.]	T [°C]	t [h]	Conversion [b,c] [%]	
			Sulfoxide	Sulfone
0.05	25	18	30	17
0.05	0–5	18	36	6
0.05 (partially soluble)	−78	72	—	—

[a] Substrate:H_2O_2:[Cat.] 1:1.1:0.01; a 10% H_2O_2 solution in THF was used.
[b] Determined by GC-MS; error ±5%.
[c] Enantiomeric excess of the sulfoxide was determined by chiral GC; in all cases sulfoxide ee = 0%.

CH_3ReO_3/H_2O_2/(+)-Tröger's base are summarized in Table 4.

In none of the studied cases did addition of the chiral base induce chirality on the product. This finding is very likely due to the dynamic behavior of the active species in solution and the weak Re–N bond strength. Furthermore, Tröger's base is oxidized to the corresponding N-oxide, as is known for other related amines (see above). Compound **2a** also does not lead to the enantioselective oxidation of the pro-chiral methyl phenyl sulfide, even if low temperatures are used (Table 5). Again the existence of dynamic exchange processes and the weak Re–N interaction in **2a** can explain this result. Nevertheless, it is very likely that a chiral N-base with a pK_b value comparable to quinuclidine will be appropriate for enantioselective oxidation catalysis. Experiments are under way to use chiral N-donors with pK_b values of the same order of magnitude or lower than quinuclidine to get chiral induction.

3. Conclusions

The Re–N interaction of N-base adducts of methyltrioxorhenium is strongly dependent on the pK_b value of the N-base. This is reflected both by structural and spectroscopic data. The strength of the Re–N bond is also reflected by the selectivity of these compounds in oxidation catalysis. The oxidizability of the N-base to the corresponding N-oxide seems to be of minor importance. However, in all cases it enhances the product yield in catalysis to use the N-bases in excess over methyltrioxorhenium. Furthermore, it is useful to generate the base adducts in situ in the catalysis solution, because most N-base adducts are much more sensitive to temperature and water than methyltrioxorhenium itself. Weak base adducts such as the chiral complex (Tröger's base)methyltrioxorhenium are not very selective in olefin epoxidation. For successful chiral catalysis N-bases with low pK_b values are more promising candidates.

4. Experimental part

All reactions were performed with standard Schlenk techniques in oxygen-free and water-free nitrogen atmosphere. Solvents were dried with standard methods and distilled under N_2. Infrared spectra were recorded on a Perkin–Elmer 1600 series FTIR spectrometer (resolution 4 cm^{-1}), the ^1H, ^{13}C and ^{17}O NMR spectra at 399.78, 100.5 and 54.25 MHz respectively on an FT-JEOL GX 400 instrument. All NMR solvents were 'freeze–pump–thaw' degassed and stored over molecular sieves before use. Elemental analyses were performed in the Microanalytical Laboratory of our institute. Mass spectra were obtained with Finnigan MAT 311A and MAT 90 spectrometers. Re_2O_7 (Degussa), quinuclidine (Aldrich), (±)-Tröger's base (Aldrich) and (+)-Tröger's base (Aldrich) were used as received. Other compounds were prepared according to literature procedures or similar methods: methyltrioxorhenium [18] and its quinuclidine, aniline, pyridine and ^{t}butylpyridine adducts [19–23].

NMR data of pure (±)-Tröger's base: ^1H NMR ($CDCl_3$, 20 °C): $\delta(^1H$, ppm) 7.08 (d, 2H, H-6, ^3J = 7.92 Hz), 7.00 (d, 2H, H-7, ^3J = 8.5 Hz), 6.74 (s, 2H, H-3), 4.68 (d, 2H, H-8, ^2J = 16.5 Hz), 4.34 (s, 2H, H-9), 4.16 (d, 2H, H-8, ^2J = 16.5 Hz), 2.26 (s, 6H, H5); ^{13}C NMR ($CDCl_3$, 20 °C): $\delta(^{13}C(^1H)$, ppm) 145.4 (C-1), 133.2 (C-2), 127.9 (C-3), 127.4 (C-4), 127.1 (C-6), 124.6 (C-7), 66.9 (C-9), 58.5 (C-8), 20.7 (C-5).

4.1. Preparation of ((5R,11R)-(+)-2,8-dimethyl-6H,12H-5,11-methanodibenzo[b,f]-[1,5]diazocine)-methyltrioxorhenium(VII) (2a)

0.25 g (1 mmol) of Tröger's base was added to a stirred solution of 0.25 g (1 mmol) methyltrioxorhenium in 10 ml diethyl ether at −45 °C. After a few minutes a yellow precipitate formed. The solution was stirred for an additional 30 min, then it was concentrated to ca. 2 ml at −25 °C in oil pump vacuum. After filtering off the mother liquor, the remaining yellow residue was washed three times with 5 ml cold diethyl ether and with 5 ml *n*-pentane. Then it was dried in oil pump vacuum. Yield 0.40 g (0.80 mmol, 80%).

^1H NMR ($CDCl_3$, 20 °C): $\delta(^1H$, ppm) 7.08 (m, 2H, H-6), 6.95 (d, 2H, H-7, ^3J = 7.9 Hz), 6.67 (s, 2H, H-3), 4.57 (d, 2H, H-8, ^2J = 16.5 Hz), 4.17 (s, 2H, H-9), 4.00 (d, 2H, H-8, ^2J = 16.5 Hz), 2.35 (s, Re–CH_3, 3H), 2.19 (s, 6H, H-5); ^{13}C NMR ($CDCl_3$, 20 °C): $\delta(^{13}C(^1H)$, ppm) 144.5 (C-1), 133.8 (C-2), 128.3 (C-3), 127.4 (C-4), 127.3 (C-6), 124.6 (C-7), 67.2 (C-9), 58.5 (C-8), 20.8 (C-5), 15.3 (*C*H_3–Re); ^{17}O NMR ($CDCl_3$, 20 °C): $\delta(^{17}O)$ 863 ppm; IR (KBr) ν = 3123 m, 2914 m, 969 s, 931 vs; CI-MS(^{187}Re) [*m/z* (rel. int. %)]: 485 ([M − CH_3]$^+$, 4), 470 ([M − C_2H_6]$^+$, 8), 250 ([CH_3ReO_3 and Tröger's base]$^+$, 100), 234 ([CH_3ReO_3–O]$^+$, 18), 218 ([CH_3ReO_3–2O]$^+$, 25); Anal. Found: C, 43.35; H, 4.29; N, 5.55; Re, 37.36. $C_{18}H_{21}N_2O_3Re$ (499.71) Calc.: C, 43.28; H, 4.24; N, 5.61; Re, 37.27%.

4.2. Crystal structure of ((5R,11R)-(+)-2,8-dimethyl-6H,12H-5,11-methanodibenzo[b,f]-[1,5]diazocine)-methyltrioxorhenium(VII)

Final lattice parameters were obtained by least-squares refinement of 25 reflections ($40.3° < 2\Theta < 48.5°$, λ = 0.70930 Å, Mo Kα_1). The space group was identified from the systematic absences: monoclinic, space group $P2_1/c$ (Int. Tab. No. 14), a = 12.816(2) Å, b = 8.339(1) Å, c = 17.055(2) Å, V = 1751.2(4) Å^3, δ_{calc} = 1.89 g cm^{-3}, Z = 4.

A yellow crystal of **2a** (size 0.51 × 0.49 × 0.54 mm^3) was mounted in a glass capillary on an Enraf–Nonius CAD4 diffractometer with Kappa geometry. Data were collected at −50 °C in the Θ-range $2° < 2\Theta < 50°$ with graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation using the ω-scan mode. All 3971 data were corrected for Lorentz and polarization terms using the SDP system [34–36]. The structure was solved by the Patterson method (SHELXS-86) [34]. All atoms were located from subsequent least-squares refinements and difference Fourier syntheses using the program CRYSTALS [35]. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were calculated and refined using the riding model. Final refinement using 2547 unique reflections ($I/\sigma(I) > 3.0$) converged at R = 0.028, R_w = 0.027. A final difference Fourier map was featureless. Additional data are recorded as supplementary material and can be obtained from Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, upon quotation of the depository number CSD-406507, the names of the authors and the journal reference for this article.

4.3. Catalysis with ((5R,11R)-(+)-2,8-dimethyl-6H,12H-5,11-methanodibenzo[b,f]-[1,5]diazocine)-methyltrioxorhenium(VII)

4.3.1. Epoxidation of olefins

Typical procedure: 0.01–0.025 g (0.04–0.1 mmol) of (+)-Tröger's base was added to a solution of 0.005 g (0.020 mmol) methyltrioxorhenium in a 3.5 M H_2O_2 solution in diethyl ether (5–8 mmol). The reaction was brought to 25 °C, and 1–2 mmol of olefin was added. The resulting mixture was then diluted with 5 ml THF, and the reaction followed by GC/MS (error ±5%).

Work up: the remaining hydrogen peroxide was destroyed with MnO_2, and the solution was filtered through Celite®.

The enantiomeric excess was determined by gas chromatography (Chrompack CP 9000) equipped with a

chiral capillary column (Macherey & Nagel, Lipodex D 50 m). The results are summarized in Table 4.

4.3.2. Sulfoxidation

Typical procedure: 0.028 g (0.11 mmol) of methyltrioxorhenium and 0.55 mmol of (+)-Tröger's base were dissolved in 4 ml of a 10% (12.3 mmol) solution of H_2O_2 in ^tBuOH and in 6 ml THF. 1.32 ml (11.2 mmol) of methyl phenyl sulfide was then added dropwise at temperatures indicated in Table 2. Conversions were determined by GC/MS (error ±5%).

Work-up: the mixture was transferred into a separatory funnel containing 30 ml of saturated aqueous solution of sodium bisulfite and 30 ml of CH_2Cl_2, and the organic phase was separated. The aqueous solution was extracted two times with 30 ml CH_2Cl_2. The combined organic phases were washed with brine, dried over $MgSO_4$, and concentrated. The sulfoxide was purified by flash chromatography. The enantiomeric excess was determined by gas chromatography (Chrompack CP 9000) equipped with a chiral capillary column (Macherey & Nagel, Lipodex D 50 m). The results are given in Table 5.

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