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Article

Oxorhenium(V) Complexes with Ketiminato Ligands: Coordination Chemistry and Epoxidation of Cyclooctene

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Rhenium(V) oxo complexes of the type $[ReOX(L)_2]$ (**1**−**7**; X = Cl, Br) containing β-ketiminate ligands (L = $CH_3C(O)CH_2C(NAr)CH_3$: Ar = Ph (APOH), 2-MePh (MPOH), 2,6-Me_2Ph (DPOH), 2,6-$^i Pr_2$Ph (DiPOH)) have been prepared by reaction of $[ReOX_3(OPPh_3)(SMe_2)]$ (X = Cl, Br) with the lithium salts of the corresponding ligands. All compounds have been spectroscopically characterized, showing $[ReOX(DiPO)_2]$ (X = Cl (**1**), Br (**5**)), $[ReOX(DPO)_2]$ (X = Cl (**2**), Br (**6**)), and $[ReOX(APO)_2]$ (X = Cl (**4**), Br (**7**)) to be isomerically pure, in contrast to complex $[ReOCl(MPO)_2]$ (**3**), which exhibits a mixture of isomers. Compounds **2**, **3**, **5**, and **7** were crystallographically characterized, showing similar octahedral coordination spheres with trans O═Re−O and cis O═Re−Cl bonds. However, the coordination of the nitrogen atoms vs each other is found to be cis or trans. Compounds **2** and **5** showed a trans-N,N configuration, for compound **3** both isomers (trans-N,N **3** and cis-N,N **3**) were structurally characterized, and **7** gave a cis-N,N configuration. Compounds **1**−**6** are catalyst precursors for the epoxidation of *cis*-cyclooctene with 3 equiv of *tert*-butyl hydroperoxide (TBHP). Yields of the formed epoxide were up to 55% with all precursors, except with **2** and **6**, where only up to 13% of epoxide was obtained under analogous conditions.

Introduction

Rhenium oxo complexes find broad application in oxidation catalysis such as in oxygen atom transfer (OAT) reactions with various non-peroxidic oxidants as well as in epoxidation reactions of olefins with peroxidic oxidants.[1−7] Rhenium(V) compounds catalyzing OAT reactivity from pyridine *N*-oxide to phosphines were thoroughly investigated by Espenson and co-workers.[8] Furthermore, rhenium(V) oxo complexes employing oxazoline-derivatized phenolate ligands were found to enable important OAT reactions as described by Abu-Omar and co-workers.[5,6,9,10] In recent years an even larger amount of research has been devoted to the investigation of epoxidation reactions of olefins catalyzed by various rhenium complexes. Mainly rhenium(VII) complexes were employed, in particular with methylrhenium(VII) oxide (MTO) and derivatives thereof.[11−14] Far less investigated were epoxidation reactions with rhenium(V) catalysts.[15−19] This is surprising, as rhenium(V) compounds feature the advantage of straightforward preparation. They represent in most cases air-stable solids, making their handling easier than their heptavalent analogues. For the first rhenium(V) oxidation catalysts, salen

(1) Herrmann, W. A.; Fischer, R. W.; Marz, D. W. *Angew. Chem., Int. Ed.* **1991**, *30*, 1638–1641.
(2) Romão, C. C.; Kühn, F. E.; Herrmann, W. A. *Chem. Rev.* **1997**, *97*, 3197–3246.
(3) Brown, S. N.; Mayer, J. M. *J. Am. Chem. Soc.* **1998**, *118*, 12119–12133.
(4) Gable, K. P.; Brown, E. C. *Organometallics* **2000**, *19*, 944–946.
(5) Arias, J.; Newland, C. R.; Abu-Omar, M. M. *Inorg. Chem.* **2001**, *40*, 2185–2192.
(6) Abu-Omar, M. M. *Chem. Commun.* **2003**, 2102–2111.
(7) Ison, E. A.; Corbin, R. A.; Abu-Omar, M. M. *J. Am. Chem. Soc.* **2005**, *127*, 11938–11939.
(8) Espenson, J. H. *Coord. Chem. Rev.* **2005**, *249*, 329–341.
(9) Abu-Omar, M. M.; McPherson, L. D.; Arias, J.; Béreau, V. M. *Angew. Chem., Int. Ed.* **2000**, *39*, 4310–4313.
(10) McPherson, L. D.; Drees, M.; Khan, S. I.; Strassner, T.; Abu-Omar, M. M. *Inorg. Chem.* **2004**, *43*, 4036–4050.
(11) Kühn, F. E.; Santos, A. M.; Herrmann, W. A. *Dalton Trans.* **2005**, 2483–2491.
(12) Kühn, F. E.; Scherbaum, A.; Herrmann, W. A. *J. Organomet. Chem.* **2004**, *689*, 4149–4164.
(13) Adam, W.; Mitchell, C. M. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 533–536.
(14) Rudolph, J.; Reddy, L. K.; Chiang, J. P.; Sharpless, K. B. *J. Am. Chem. Soc.* **1997**, *119*, 6189–6190.
(15) Herrmann, W. A.; Rauch, U. M.; Artus, G. R. J. *Inorg. Chem.* **1996**, *35*, 1988–1991.
(16) Kühn, F. E.; Rauch, M. U.; Lobmaier, G. M.; Artus, G. R. J.; Herrmann, W. A. *Chem. Ber.* **1997**, *130*, 1427–1431.
(17) Deloffre, A.; Halut, S.; Salles, L.; Brégeault, J.-M.; Gregorio, J. R.; Denise, B.; Rudler, H. *J. Chem. Soc., Dalton Trans.* **1999**, 2897–2898.
(18) Lobmaier, G. M.; Guido, D.; Frey, R. D.; Dewhurst, E. H.; Herrmann, W. A. *Organometallics* **2007**, *26*, 6290–6299.
(19) Sachse, A.; Mösch-Zanetti, N. C.; Lyashenko, G.; Wielandt, J. W.; Most, K.; Magull, J.; Dall'Antonia, F.; Pal, A.; Herbst-Irmer, R. *Inorg. Chem.* **2007**, *46*, 7129–7135.

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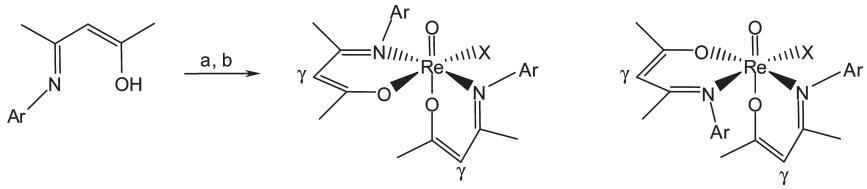
Scheme 1.[a]



DiPOH Ar = 2,6-$^{i}Pr_2$Ph
DPOH Ar = 2,6-Me_2Ph
MPOH Ar = 2-MePh
APOH Ar = Ph

***trans*-N,N**
1 X= Cl, DiPO, 64%
2 X= Cl, DPO, 83%
3 X= Cl, MPO, 17%
5 X= Br, DiPO, 81%
6 X= Br, DPO, 76%

***cis*-N,N**
3 X= Cl, MPO, 33%
4 X= Cl, APO, 45%
7 X= Br, APO, 41%

[a] Legend: (a) *n*-BuLi, heptane, crude; (b) $[ReOX_3(OPPh_3)(SMe_2)_2]$ (X = Cl, Br), toluene, reflux, 2 h.

type ligands were chosen, presumably due to the success of such ligands in other oxidation reactions.[20,21] Recently, two rhenium(V) catalysts with non-phenolate ligands were reported in the literature.[18,19] However, the rhenium(V) systems investigated so far show significantly lower activity or productivity than rhenium(VII) systems. In addition, catalyst deactivation is often observed, in particular if Re(V) complexes of the type $[ReOX_2L]$ (X = halide, L = alcoholate or phenolate type ligand) are employed. Lobmaier et al. found that substitution by a second alcoholate ligand, forming the complexes $[ReOX(L)_2]$ significantly increased the stability of the complexes in catalytic epoxidation.[18] This encouraged us to further investigate our rhenium(V) complexes employing Schiff base ligands derived from acetylacetone.

The coordination chemistry of rhenium(V) oxo complexes with acetylacetone-derived Schiff base ligands has been explored to only a limited extent. Jurisson and coworkers[22,23] have investigated the reactivity of some bidentate and tetradentate ligand systems toward rhenium(V) oxo precursors, revealing unexpected compounds. We recently reported the coordination chemistry of rhenium(V) oxo complexes with a series of β-ketimininate ligands and their application in epoxidation reactions. We found that complexes of the type $[ReOCl_2L(PPh_3)]$ and $[NBu_4][ReOCl_3L]$, where L represents β-ketiminate ligands, can be prepared in high yields. With these precursors, complexes of the type $[ReOCl(L)_2]$ remained elusive. $[ReOCl_2L(PPh_3)]$ proved to be active in the epoxidation of *cis*-cyclooctene with *tert*-butyl hydroperoxide (TBHP). However, the catalyst was found to deactivate after an initial high reaction rate.

Here, we report the reaction of the more reactive precursors $[ReOX_2(OPPh_3)(SMe_2)]$ (X = Cl, Br) with a series of β-ketiminato ligands, allowing the preparation of disubstituted rhenium(V) oxo complexes of the type $[ReOCl(L)_2]$. Their potential as epoxidation catalysts for *cis*-cyclooctene was investigated.

Results and Discussion

Syntheses of the Compounds. The desired complexes of the type $[ReOX(L)_2]$ (**1**−**7**; X = Cl, Br) were prepared by metathesis reactions between $[ReOX_3(OPPh_3)(SMe_2)]$ (X = Cl, Br)[24,25] and the lithium salts of the β-ketimines APOH, MPOH, DPOH, and DiPOH. The ligands were readily available in good yields by condensation of acetylacetone with corresponding amines according to known procedures.[26] Formation of their lithium salts was achieved by the use of *n*-butyllithium (*n*-BuLi) in hexane. Treatment of the lithium salts APOLi, MPOLi, DPOLi, and DiPOLi with the respective metal precursor in refluxing toluene gave the desired complexes in medium to good yields and were purified from chloroform/pentane to give green crystals of the products (Scheme 1). Milder reaction conditions, e.g. at room temparture or lower boiling solvents, gave lower conversions. Performing the complexation with metal precursors such as $[NBu_4][ReOCl_4]$ and $[ReOX_3(PPh_3)_2]$ (X = Cl, Br) under various conditions gave products containing one ligand moiety attached to the rhenium only.[19]

However, the synthetic procedure described here using $[ReOX_3(OPPh_3)(SMe_2)]$ (X = Cl, Br) as the metal precursor and lithium salts of the ligands for the delivery of the desired complexes **1**−**7** proceeded smoothly under reflux conditions. Released compounds such as LiX (X = Cl, Br), Me_2S, and $OPPh_3$ could easily be removed during the workup procedure, and complexes **1**−**7** showed high stability in both the solid and dissolved states for several months at ambient temperature.

Complexes **1**−**7** were characterized by IR spectroscopy, elemental analyses, and NMR spectroscopy, and for compounds **2**, **3**, **5**, and **7** single crystal X-ray diffraction analyses were performed. The IR spectra of the complexes gave a characteristic stretching frequency for the Re=O moiety,[18,22,23,27,28] and elemental analyses confirmed the basic formula of $[ReOXL_2]$ (X = Cl, Br) for all compounds.

Several isomers can in principle be formed, as shown in Figure 1.

Diastereoisomers of types A and B were expected to be formed preferably, since most complexes with Schiff base ligands are reported where the oxygen atom of one ligand is coordinated trans to the Re=O unit.[16] This was supported by ^{1}H NMR spectroscopy of the complexes where inequivalent chemical shifts for the γ-protons of the

(20) Jacobsen, E. N.; Zhang, W.; Muci, A. R.; Ecker, J. R.; Deng, L. *J. Am. Chem. Soc.* **1991**, *113*, 7063–7064.
(21) Yang, J. Y.; Nocera, D. G. *J. Am. Chem. Soc.* **2007**, *129*, 8192–8198.
(22) Benny, P. D.; Barnes, C. L.; Piekarski, P. M.; Lydon, J. D.; Jurisson, S. S. *Inorg. Chem.* **2003**, *42*, 6519–6527.
(23) Benny, P. D.; Green, J. L.; Engelbrecht, H. P.; Barnes, C. L.; Jurisson, S. S. *Inorg. Chem.* **2005**, *44*, 2381–2390.
(24) Grove, D. E.; Wilkinson, G. J. *J. Chem. Soc. A* **1966**, 1224–1230.
(25) Sherry, B. D.; Loy, R. N.; Toste, F. D. *J. Am. Chem. Soc.* **2004**, *126*, 4510–4511.
(26) Martin, D. F.; Janusonis, G. A.; Martin, B. B. *J. Am. Chem. Soc.* **1961**, *83*, 73–75.
(27) McPherson, L. D.; BeReau, V. M.; Abu-Omar, M. M.; Urgrinova, V. P.; Lihung, T.; Scheroi, D.; Brown, S. N. *Inorg. Synth.* **2004**, *34*, 54–59.
(28) Nguyen, H. H.; Grewe, J.; Schroer, J.; Kuhn, B.; Abram, U. *Inorg. Chem.* **2008**, *47*, 5136–5144.

attached ligands in the range between 5 and 6 ppm were obtained. The structural assignment (type A or B) of the complexes could be confirmed by single-crystal X-ray structure analyses (vide infra).

Proton NMR spectroscopic analyses of compounds **1**, **2**, and **4** together with their bromo counterparts **5**−**7** revealed the complexes to be isomerically pure, as indicated by a total of two resonances for the γ-proton of the asymmetrically arranged ligands. Interestingly, the ^{1}H NMR spectra of **4** and **7** with the least sterically demanding ligand (APO) gave an unexpected doublet at ~4.80 ppm, which was found to be of aromatic nature by correlation spectra (H,H-COSY and HSQC). Such an upfield-shifted aromatic proton was not observed in the ^{1}H NMR spectra of compounds **1**, **2**, **5**, and **6**. Single-crystal X-ray diffraction of **2**, **5**, and **7** allowed the assignment showing the complexes exhibiting the upfield-shifted aromatic proton to be cis-N,N isomers (**4**, **7**) whereas the others to be trans-N,N isomers (**1**, **2**, **5**, and **6**). Presumably

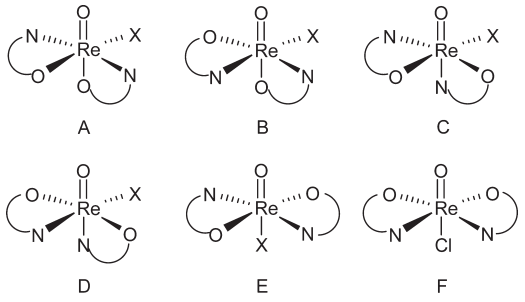


Figure 1. Isomers for complexes of the type $[ReOX(L)_2]$ (X = Cl, Br) (L = bidentate β-ketiminate).

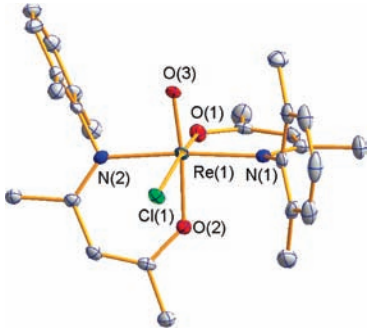


Figure 2. Molecular view of $[ReOCl(DPO)_2]$ (**2**) with selected atom numbering. Hydrogen atoms are omitted for clarity.

the shifted doublets belong to the ortho protons pointing toward the nearby located aromatic ring of the second ligand (Figures 3 and 4). ^{1}H NMR spectroscopy of the crude complex **3**, with sterically less demanding ligands attached to the rhenium moiety, showed the presence of two isomers, as in the region of the γ-protons four singlets were observed. Furthermore, a doublet at 4.91 ppm is found, indicating one of the two to be the cis-N,N isomer. On crystallization of crude **3** from a mixture of chloroform/pentane single crystals of the cis-N,N isomer were obtained, as shown by X-ray crystallography. The ^{1}H NMR spectrum of these crystals showed a doublet at 4.91 ppm, consistent with the finding for compounds **4** and **7**. On prolonged standing of the mother liquor, a second type of crystals was obtained for which X-ray diffraction analysis revealed the trans-N,N coordinated compound **3**, and in the ^{1}H NMR spectrum the doublet at 4.91 ppm was absent. These findings reveal a strong influence of the steric demand of the ligand on the complex structure. Thus, the bulky ligands DiPO and DPO gave trans-N,N complexes, whereas the APO ligand gave cis-N,N. The MPO ligand with only one methyl group at the aromatic ring exhibits an intermediate bulkiness, leading to both structures in solution.

Molecular Structures of the Compounds. Structures of compounds **2**, **3**, **5**, and **7** were determined by X-ray diffraction analyses. Molecular views of **2**, **3**, and **7** are shown in Figures 2−4, crystallographic data are presented in Table 1, and selected bond lengths and angles are given in Tables 2 and 3. Furthermore, the molecular structure of complex **5** confirmed the connectivity showing the trans-N,N isomer; however, the quality of the data set did not allow a discussion of bond lengths and angles.

Compound **2**, $[ReOCl(DPO)_2]$, was found to be the trans-N,N isomer of type A; complex **3**, $[ReOCl(MPO)_2]$, gave two types of crystals that proved to be the trans-N,N (type A) and the cis-N,N (type B) isomers. Compound **7**, $[ReOBr(APO)_2]$, also gave two types of crystals, both showing it to be the cis-N,N isomer (type B), but in a monoclinic or triclinic modification (Figure 4). All complexes show a six-coordinate rhenium atom with distorted-octahedral coordination spheres and trans O−Re=O and cis Cl−Re=O bonds. This is due to a strong trans effect of the oxo group, forcing the harder oxygen atom of the NO ligand into a trans position.[16] The equatorial plane of the complexes consists of the two nitrogen atoms, the halide atom, and an oxygen atom from the ligand. Differences in the structures result from

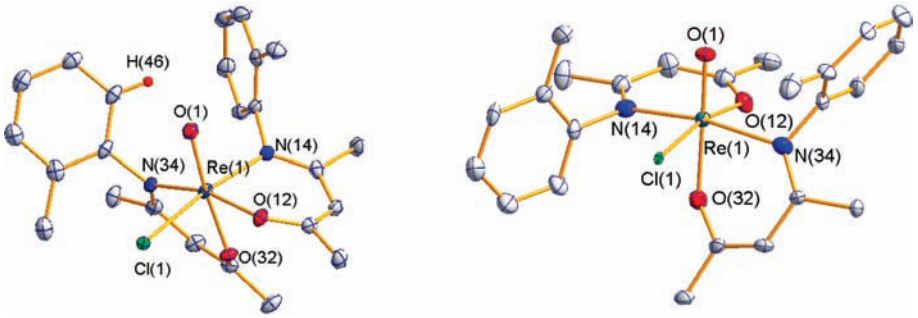


Figure 3. Molecular view of *cis*-*N*,*N*-$[ReOCl(MPO)_2]$ (**3**) and *trans*-*N*,*N*-$[ReOCl(MPO)_2]$ (**3**) with selected atom numbering. Hydrogen atoms are omitted for clarity, except for hydrogen H(46) pointing toward the aromatic ring.

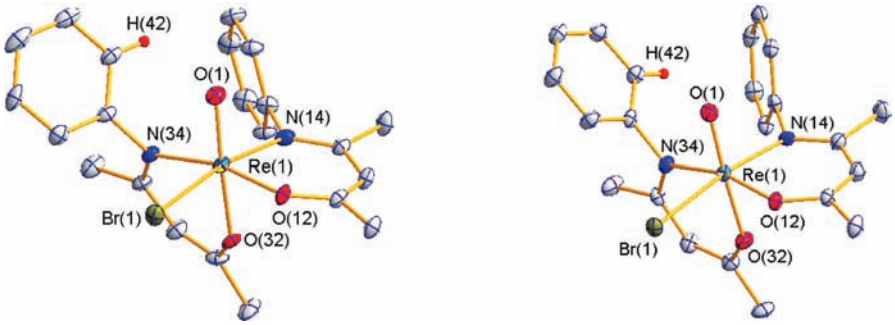


Figure 4. Molecular view of [ReOBr(APO)$_2$] (**7**) in monoclinic (left) and triclinic (right) modifications with selected atom numbering. Hydrogen atoms are omitted for clarity, except for hydrogen H(42) pointing toward the aromatic ring.

Table 1. Crystallographic Data for *trans*-*N*,*N*-[ReOCl(DPO)$_2$] (**2**), *cis*-*N*,*N*-[ReOCl(MPO)$_2$] (**3**), *trans*-*N*,*N*-[ReOCl(MPO)$_2$] (**3**), *cis*-*N*,*N*-[ReOBr(APO)$_2$] (**7**)

	trans-*N*,*N*-**2**	*cis*-*N*,*N*-**3**	*trans*-*N*,*N*-**3**	*cis*-*N*,*N*-**7** monoclinic	*cis*-*N*,*N*-**7** triclinic
formula	$C_{26}H_{32}ClN_2O_3Re$	$C_{24}H_{28}ClN_2O_3Re$	$C_{24}H_{28}ClN_2O_3Re$	$C_{22}H_{24}BrN_2O_3Re$	$C_{22}H_{24}BrN_2O_3Re$
fw	642.19	614.13	614.13	630.54	630.54
color/habit	green/block	green/needle	green/block	green/block	green/block
cryst size (mm^3)	0.38 × 0.22 × 0.20	0.30 × 0.10 × 0.08	0.22 × 0.22 × 0.14 mm	0.22 × 0.22 × 0.14	0.25 × 0.20 × 0.11
cryst syst	monoclinic	monoclinic	orthorhombic	monoclinic	triclinic
space group	*C*2/*c*	$P2_1/n$	$Pna2_1$	$P2_1/c$	$P\bar{1}$
a (Å)	33.316(7)	11.4488(17)	13.496(2)	13.2817(19)	9.687(2)
b (Å)	7.7181(15)	32.097(4)	10.718(2)	9.2166(12)	9.741(2)
c (Å)	22.064(4)	13.942(3)	16.288(3)	18.275(2)	13.447(3)
α (deg)	90	90	90	90	72.491(18)
β (deg)	119.54(3)	111.766(14)	90	103.686(12)	71.40(2)
γ (deg)	90	90	90	90	69.02(2)
V (Å^3)	4936.1(17)	4758.0(14)	2356.1(7)	2173.6(5)	1097.6(4)
Z	8	8	4	4	2
T (K)	100	95	95	95	95
D_{calcd} (g cm^{-3})	1.728	1,715	1.731	1.927	1.908
μ (mm^{-1})	5.062	5.247	5.298	7.454	7.381
abs cor type/program	multiscan	empirical/XABS 2[b]	empirical/XABS 2[b]	empirical/XABS 2[b]	empirical/XABS 2[b]
F(000)	2544	2416	1208	1216	608
θ range (deg)	1.88−26.36	2.70−30.00	2.50−30.00	2.72−30.00	2.52−30.00
limiting indices	$-41 \le h \le 41$	$-16 \le h \le 15$	$-18 \le h \le 18$	$-2 \le h \le 18$	$-13 \le h \le 13$
	$-9 \le k \le 9$	$-45 \le k \le 45$	$-15 \le k \le 15$	$-12 \le k \le 3$	$-13 \le k \le 4$
	$-27 \le l \le 27$	$-2 \le l \le 19$	$-22 \le l \le 22$	$-25 \le l \le 24$	$-18 \le l \le 18$
no. of rflns collected	18 464	15 895	8047	7252	7414
no. of indep rflns, R_{int}	5011, 0.0647	13 862, 0.341	4252, 0.0400	6316, 0.0353	6356, 0.0349
no. of obsd rflns, $I > 2\sigma(I)$	4455	11481	3521	5471	5975
Flack param			0.07(2)		
no. of data/restraints/params	5011/0/306	13 862/0/589	4252/1/ 295	6316/0/274	6356/0/274
R1/wR2 ($I > 2\sigma(I)$)[a]	0.0373/0.0820	0.0434/0.0962	0.0476/0.1218	0.0499/0.1298	0.0413/0.1097
R1/wR2 (all data)[a]	0.0457/0.0848	0.0572/0.1033	0.0580/0.1292	0.0585/0.1381	0.0441/0.1122
GOF (on F^2)[a]	1.027	1.057	1.075	1.051	1.062
largest diff peak/hole (e Å^{-3})	4.315 and −1.114[c]	2.057 and −1.554[c]	2.946 and −3.138[c]	5.146 and −3.463[c]	2.964 and −3.621[c]

[a] $R = \sum(||F_o| - |F_c||)/\sum|F_o|$. wR2 = $\{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. GOF = $\{\sum[w(F_o^2 - F_c^2)^2]/(n-p)\}^{1/2}$. [b] Reference 34. [c] Residual electron density is centered around the rhenium atom.

Table 2. Selected Bond Distances (Å) and Angles (deg) for *trans*-*N*,*N*-[ReOCl(DPO)$_2$] (**2**)

Re(1)−O(1)	2.035(3)	Re(1)−N(1)	2.096(4)
Re(1)−O(2)	2.001(3)	Re(1)−N(2)	2.128(4)
Re(1)−O(3)	1.685(3)	Re(1)−Cl(1)	2.397(1)
O(3)−Re(1)−O(2)	174.0(1)	N(1)−Re(1)−N(2)	172.4(1)
O(1)−Re(1)−Cl(1)	166.6(1)	O(3)−Re(1)−Cl(1)	93.3(1)

the coordination of the nitrogen atoms of the ligands to the rhenium, depending on substituents present at the aromatic ring of the *β*-ketiminates.

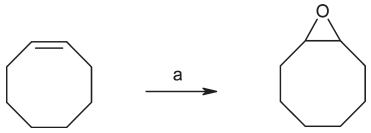
All compounds gave bond lengths for Re=O (1.685(3) Å, **2**; 1.688(4) Å, *cis*-*N*,*N*-**3**; 1.704(7) Å, *trans*-*N*,*N*-**3**; 1.689(4) Å, **7** monoclinic; 1.676(4) Å, **7** triclinic) and Re−X (X = Br, Cl: 2.3973(13) Å, **2**; 2.4327(12) Å, *cis*-*N*,*N*-**3**; 2.4521(19) Å, *trans*-*N*,*N*-**3**; 2.5393(7) Å, **7** monoclinic; 2.5502(7) Å, **7** triclinic) within the expected range for other [ReOXL$_n$] (X = Cl, Br) structures.[10,16,18,29] In complex **2**, the two nitrogen atoms N(1) and N(2) are coordinated in positions trans to each other (Figure 2), presumably due to the high steric demand of the methyl groups attached to the aromatic ring with a N(1)−Re(1)−N(2) angle of 172.44(14)°. The ligand MPO with only one methyl group at the aromatic ring afforded the formation of isomers on complexation with the rhenium metal precursor to give complex **3** in cis-N,N and trans-N,N configurations (N14 and N34) (Figure 3). The N(14)−Re(1)−N(34) angle of 166.5(3)° for the trans isomer is smaller compared to that for complex **2**. The trans isomers shows a N(14)−Re(1)−N(34) angle of 93.11(16)°, which is comparable to those for complex **7**, with a

(29) Luo, H.; Rettig, S. J.; Orvig, C. *Inorg. Chem.* **1993**, *32*, 4491–4497.

Table 3. Selected Bond Distances (Å) and Angles (deg) for *cis*-*N*,*N*-[ReOCl(MPO)$_2$] (**3**), *trans*-*N*,*N*-[ReOCl(MPO)$_2$] (**3**), and *cis*-*N*,*N*-[ReOBr(APO)$_2$] (**7**)

	cis-*N*,*N*-**3**	*trans*-*N*,*N*-**3**	*cis*-*N*,*N*-**7** monoclinic	*cis*-*N*,*N*-**7** triclinic
Re(1)−O(1)	1.688(4)	1.704(7)	1.689(4)	1.676(4)
Re(1)−Cl(1)	2.433(1)	2.452(2)		
Re(1)−Br(1)			2.5393(7)	2.5502(7)
Re(1)−O(12)	2.037(4)	2.017(7)	2.015(4)	2.016(3)
Re(1)−O(32)	1.992(3)	2.013(8)	2.016(4)	2.012(4)
Re(1)−N(14)	2.125(4)	2.115(8)	2.134(5)	2.095(4)
Re(1)−N(34)	2.134(4)	2.131(8)	2.135(5)	2.137(4)
O(1)−Re(1)−Cl(1)	97.9(1)	90.7(2)		
O(1)−Re(1)−Br(1)			100.7(2)	97.1(1)
O(1)−Re(1)−O(32)	171.1(2)	174.2(3)	169.6(2)	173.3(2)
N(14)−Re(1)−Br(1)			169.5(1)	171.9(1)
N(14)−Re(1)−Cl(1)	172.4(1)			
O(12)−Re(1)−N(34)	163.9(2)		166.3(2)	165.2(2)
O(12)−Re(1)−Cl(1)		169.1(2)		
N(14)−Re(1)−N(34)		166.5(3)		

Scheme 2.[a]



[a] Legend: (a) TBHP, Re(V) (2 mol %), $CHCl_3$, 50 °C.

N(14)−Re(1)−N(34) angle of 94.39(19)° for the monoclinic and 94.63(16)° for the triclinic form, respectively. The two isomers present in the $CDCl_3$ solution of **7** are expected to be the cis-N,N and trans-N,N isomers; however, crystallization attempts afforded only crystals which were shown to be of the cis-N,N structure (type B) in triclinic and monoclinic modifications. The isolation of the second isomer proved unsuccessful.

Catalytic Epoxidations. Few rhenium(V) complexes are known to show catalytic activity in the epoxidation of *cis*-cyclooctene with *tert*-butyl hydroperoxide (TBHP).[15,18] Recently, we investigated complexes of the type [ReOCl$_2$(DPO)(PPh$_3$)] in the reaction of *cis*-cyclooctene with TBHP.[19] The catalyst exhibits catalytic conversion to the epoxide but was accompanied by decomposition of the catalyst. Similar results were reported by Lobmaier et al., who found their monosubstituted complexes [ReOCl$_3$L]$^-$ (L = bis(alkyl/aryl)-2-pyridylalcoholate) to be deactivated quickly.[18] This indicated that monodentate ligands such as the chlorine atoms are likely lost and prompted us to investigated the disubstituted ketiminato rhenium(V) complexes described here.

The catalytic reactions were performed in chloroform solution at 50 °C by the use of 2 mol % of the corresponding catalyst and a 3-fold excess of the peroxide (Scheme 2). The conversion to the epoxide was monitored by GCMS analyses; samples were taken every 1 h and quenched with MnO_2 before analyses. The prepared chloro complexes **1**−**4** as well as the two bromo counterparts **5** and **6** were tested for their catalytic activity (Figure 5). A blank test in the absence of catalysts gave no conversion.

Complexes **2** and **6** gave low conversion to the corresponding epoxide (13% yield), which is in contrast to our previous findings where the monosubstituted analogue [ReOCl$_2$(DPO)(PPh$_3$)] gave 50% conversion to the epoxide.[19] Apparently, catalytically active species are formed in both cases, but that obtained from **2** decomposes more quickly compared to that of the monosubstituted

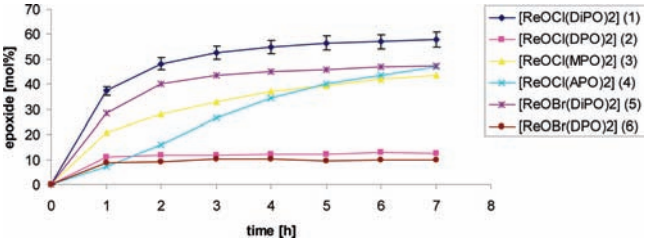


Figure 5. Epoxidation of *cis*-cyclooctene using the catalysts **1**−**6**.

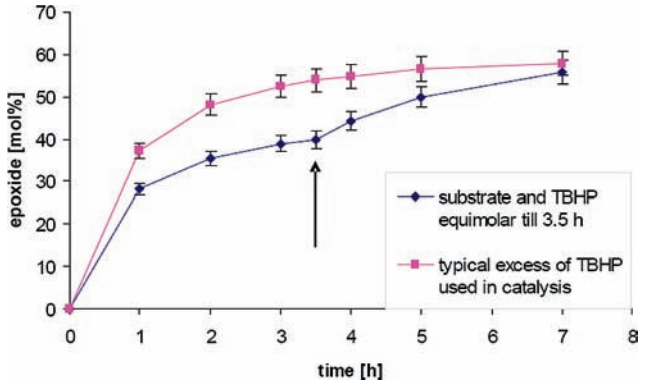


Figure 6. Epoxidation of *cis*-cyclooctene using the catalyst [ReOCl(DiPO)$_2$] (**1**). The arrow indicates the addition of 2 equiv of TBHP.

complex for as yet unclear reasons. Complexes **1**, **3**, **4**, and **5** gave the epoxide in good yields (up to 55%) in all cases, indicating that the remaining halogenide in the compound has no influence on the catalytic reaction.

Furthermore, Figure 6 shows the epoxidation progress monitored by GCMS for compound **1** with different starting concentrations of the oxidant. The formation of the epoxide is fast within 1 h, after which a decrease on prolonged reaction time is noticed. When an equimolar amount of TBHP was used in the epoxidation reaction, the rate of formation was comparable to that obtained with a 3-fold excess of TBHP but giving lower conversion (35 mol %). The yield could be improved to ∼55 mol % on addition of 2 equiv of TBHP, indicating unproductive reduction of the peroxide during catalysis.

The formation of a white precipitate was noticed during the epoxidation reaction. Presumably, the precipitate is a perrhenate salt formed by decomposition of the rhenium(V) complexes. Similar behavior has been observed

previously.[18,19] For this reason, we tested sodium perrhenate as a catalyst in the epoxidation reaction under analogous conditions (3-fold excess of H_2O_2) and found a 27 mol % yield of the corresponding epoxide. However, monitoring the reaction revealed a slow increase of the yield over a period of 7 h without the observation of a higher activity in the initial phase of the catalysis. This points to a different catalytic species in the system reported here. In the well-explored OAT reactions employing rhenium(V) dithiolate complexes, the formation of a dioxorhenium(VII) intermediate is believed to be the driving force for the transfer.[8] Whether this applies here is as yet unclear, as the isolation of the any species after the catalysis is elusive. A rhenium(VII) species as the active catalyst was suggested in the literature,[15] in analogy to the identified $[(CH_3)Re(O_2)_2O]$ reaction product of methylrhenium trioxide (MTO) with H_2O_2.[2] Under the same conditions, complex **1** was tested as a catalyst in the epoxidation of styrene with TBHP, but no oxidation was observed.

Conclusion

Rhenium(V) oxo complexes of the type $[ReOX(L)_2]$ (**1**−**7**; X = Cl, Br) containing β-ketiminate ligands were prepared and characterized. Depending on the steric demand at the nitrogen, compounds **1**−**7** form two different isomers. Thus, **1**, **2**, **5**, and **6** exist as the trans-N,N isomer in solution and compounds **4** and **7** as the cis-N,N isomer, whereas **3** exhibits a mixture of isomers. Formation of either trans-N,N or cis-N,N complexes was confirmed by the determination of the solid-state structures by X-ray diffraction analysis. In addition, ^{1}H NMR spectroscopy proved to be an easy tool for the determination of the nature of the isomer by the presence of an indicative upfield-shifted aromatic proton resonance for the cis-N,N isomer. Compounds **1**−**6** are catalyst precursors for the epoxidation of *cis*-cyclooctene with 3 equiv of TBHP. Yields of the formed epoxide were up to 55% with all precursors. GCMS monitoring of the catalytic reaction employing **1** under various conditions showed fast initial catalysis followed by deactivation when reaching approximately 55% yield.

Experimental Section

Materials. Syntheses were performed under an argon atmosphere using common Schlenk techniques with subsequent workup under ambient conditions. The metal precursors[24,25] $[ReOCl_3(OPPh_3)(SMe_2)]$ and $[ReOBr_3(OPPh_3)(SMe_2)]$ as well as the ligands[26] APOH, MPOH, DPOH, and DiPOH were prepared essentially according to known procedures. Chemicals were purchased from commercial sources and were used without further purification. Solvents were purified via a Pure-Solv Solvent Purification System. ^{1}H NMR spectra were recorded with Varian Bruker (360 MHz) instruments. Chemical shifts are given in ppm and are referenced to partially protonated solvent or internal standard. Signals are described as s (singlet), d (doublet), dd (double doublet), t (triplet), h (heptet), and m (multiplet), and coupling constants (*J*) are given in hertz (Hz). Elemental analyses were carried out using a Heraeus Vario Elementar automatic analyzer. Mass spectra were recorded with an Agilent 5973 MSD-Direct Probe using the EI ionization technique. Samples for infrared spectroscopy were prepared as KBr pellets and measured on a Perkin-Elmer FT-IR 1725X spectrometer.

X-ray Structure Determination. For X-ray structure analyses the crystals were mounted onto the tip of glass fibers, and data collection was performed at low temperature using graphite-monochromated Mo Kα radiation (0.710 73 Å) with a Bruker-AXS SMART APEX CCD diffractometer (for compound **2**) or with a STOE four-circle diffractometer with a scintillation counter (for compounds **3** and **7**). The data were reduced to F_o^2 and corrected for absorption effects with SAINT[30] and SADABS[31] (for compound **2**), or an empirical absorption correction[32] was applied (for compounds **3** and **7**). The structures were solved by direct methods (compounds **2** and **3**) or by Patterson superposition procedures where direct methods failed (compounds **7**) and refined by full-matrix least-squares methods (SHELXL97).[33] All non-hydrogen atoms were refined with anisotropic displacement parameters without any constraints. All hydrogen atoms were located in calculated positions to correspond to standard bond lengths and angles. Common isotropic displacement parameters were refined for the H atoms bonded to the same C atom or to the same phenyl ring. All diagrams were drawn with 50% probability thermal ellipsoids, and all hydrogen atoms were omitted for clarity. Crystallographic data (excluding structure factors) for the structures of compounds **2**, **3**, and **7** reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-734779 (*cis*-*N*,*N*-**2**), CCDC 734088 (*cis*-*N*,*N*-**3**), CCDC 734089 (*trans*-*N*,*N*-**3**), 734090 (*cis*-*N*,*N*-**7** monoclinic), 734091 (*cis*-*N*,*N*-**7** triclinic). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, (internat.) +44-1223/336-033; E-mail, deposit@ccdc.cam.ac.uk). A summary of the crystallographic data is given in Table 1. GCMS measurements were performed on an Agilent 7890 A with an Agilent 19091J-433 column coupled to an Agilent 5975 C mass spectrometer. For each quantitative analysis linear regression calibration functions were made for *cis*-cyclooctene, cyclooctene oxide, and di-*n*-butyl ether; $R_2 \geq 0.998$.

General Procedure. The lithium salt of the ligand (APOLi, MPOLi, DPOLi, DiPOLi) in toluene was added to a suspension of the respective rhenium precursor $[ReOX_3(OPPh_3)(SMe_2)]$ (X = Cl, Br) in toluene. The suspension was heated under reflux for 2 h to give a dark green solution. Removal of undissolved material and evaporation of the organic layer gave a solid which was recrystallized from a mixture of $CHCl_3$/pentane (1 + 4 v/v). The obtained solids were subsequently washed with heptane to give the desired products.

$[ReOCl(DiPO)_2]$ (1). A solution of DiPOLi (0.082 g, 0.31 mmol) in toluene (20 mL) was added to a suspension of $[ReOCl_3(OPPh_3)(SMe_2)]$ (0.10 g, 0.16 mmol) in toluene (30 mL). The preceding general procedure gave 0.075 g (64%) of green crystals. ^{1}H NMR ($CDCl_3$, 360 MHz, ppm): δ 1.10, 1.27 (2 m, 24H, CH_3), 1.94 (s, 3H, CH_3), 2.24 (s, 3H, CH_3), 2.47 (s, 3H, CH_3), 2.64 (h, $^3J_{H-H}$ = 6.8 Hz, 1H, C*H*), 2.77 (s, 3H, CH_3), 3.28 (h, $^3J_{H-H}$ = 6.9 Hz, 1H, C*H*), 3.59 (h, $^3J_{H-H}$ = 6.8 Hz, 1H, C*H*), 3.78 (h, $^3J_{H-H}$ = 6.8 Hz, 1H, C*H*), 5.35 (s, 1H, C*H*), 5.63 (s, 1H, C*H*), 7.22 (m, 6H, Ar). IR (KBr, cm^{-1}): 1610, 1570, 1526, 1358, 1274, 1168, 972, 936, 800, 758, 544. MS (EI, *m*/*z* (%)): 754 (23) [M$^+$]. Anal. Calcd for $C_{34}H_{48}ClN_2O_3Re$ C, 54.1; H, 3.84; N, 3.71. Found: C, 54.2; H, 3.87; N, 3.68.

$[ReOCl(DPO)_2]$ (2). A solution of DPOLi (0.065 g, 0.331 mmol) in toluene (20 mL) was added to a suspension of $[ReOCl_3(OPPh_3)(SMe_2)]$ (0.10 g, 0.16 mmol) in toluene (30 mL). The preceding general procedure gave 0.085 g (83%) of green crystals. ^{1}H NMR ($CDCl_3$, 360 MHz, ppm): δ 1.89 (s, 3H,

(30) *SAINTPLUS: Software Reference Manual, Version 6.45*; Bruker-AXS: Madison, WI, 1997−2003.
(31) Blessing, R. H. *Acta Crystallogr., Sect. A* **1995**, *51*, 33–38. *SADABS: Version 2.1*; Bruker AXS, Madison, WI, **1998**.
(32) Parkin, S; Moezzi, B.; Hope, H. *J. Appl. Crystallogr.* **1995**, *28*, 53–56.
(33) Sheldrick, G. M. *SHELX97 Programs for Crystal Structure Analysis* (*Release 97-2*); Universität Göttingen,Göttingen, Germany, **1998**.
(34) Parkin, S.; Moezzi, B.; Hope, H. *J. Appl. Crystallogr.* **1995**, *53*, 53–56.

CH_3), 2.01 (s, 3H, CH_3), 2.14 (s, 3H, CH_3), 2.32 (s, 3H, CH_3), 2.35 (s, 3H, CH_3), 2.42 (s, 3H, CH_3), 2.48 (s, 3H, CH_3), 2.74 (s, 3H, CH_3), 5.30 (s, 1H, C*H*), 5.79 (s, 1H, C*H*), 7.03 (m, 4H, Ar), 7.14 (d, $^3J_{H-H}$ = 7.5 Hz, 2H, Ar). IR (KBr, cm^{-1}): 1570, 1510, 1436, 1372, 1268, 1184, 1120, 970, 938, 912, 746, 696, 550. MS (EI, *m*/*z* (%)): 642 (83) [M^+]. Anal. Calcd for $C_{26}H_{32}ClN_2O_3Re \cdot 0.8OPPh_3$: C, 56.1; H, 5.13; N, 3.24. Found: C, 56.2; H, 5.04; N, 2.81.

[ReOCl(MPO)$_2$] (3). A solution of MPOLi (0.059 g, 0.30 mmol) in toluene (20 mL) was added to a suspension of $[ReOCl_3(OPPh_3)(SMe_2)]$ (0.10 g, 0.15 mmol) in toluene (30 mL). The preceding general procedure gave 0.03 g (*cis*-*N*,*N*-**3**, 33%) and 0.016 g (*trans*-*N*,*N*-**3**, 17%) of green crystals. *cis*-*N*,*N*-**3**: ^{1}H NMR ($CDCl_3$, 360 MHz, ppm) δ 1.79 (s, 3H, CH_3), 2.17 (s, 3H, CH_3), 2.40 (s, 3H, CH_3), 2.46 (s, 3H, CH_3), 2.68 (s, 3H, CH_3), 2.93 (s, 3H, CH_3), 4.91 (d, $^3J_{H-H}$ = 8.1 Hz, 1H, Ar), 5.21 (s, 1H, C*H*), 5.97 (s, 1H, C*H*), 6.69 (m, 2H, Ar), 6.93 (m, 1H, Ar), 7.09 (m, 3H, Ar), 7.33 (d, $^3J_{H-H}$ = 7.8 Hz, 1H, Ar); IR (KBr, cm^{-1}) 1570, 1510, 1468, 1438, 1378, 1270, 1180, 1120, 970, 938, 908, 748, 702, 694, 564; MS (EI, *m*/*z* (%)) 614 (97) [M^+]. Anal. Calcd for $C_{24}H_{28}ClN_2O_3Re$: C, 46.9; H, 4.60; N, 4.56. Found: C, 47.0; H, 4.41; N, 4.32. *trans*-*N*,*N*-**3**: ^{1}H NMR ($CDCl_3$, 360 MHz, ppm) δ 1.93 (s, 3H, CH_3), 2.07 (s, 3H, CH_3), 2.18 (s, 3H, CH_3), 2.45 (s, 3H, CH_3), 2.52 (s, 3H, CH_3), 2.79 (s, 3H, CH_3), 5.29 (s, 1H, C*H*), 5.82 (s, 1H, C*H*), 7.07 (m, 3H, Ar), 7.14 (m, 3H, Ar), 7.24 (m, 2H, Ar). MS (EI, *m*/*z* (%)) 614 (97) [M^+]. Anal. Calcd for $C_{24}H_{28}ClN_2O_3Re$: C, 46.9; H, 4.60; N, 4.56. Found: C, 47.0; H, 4.41; N, 4.32.

[ReOCl(APO)$_2$] (4). A solution of APOLi (0.060 g, 0.33 mmol) in toluene (20 mL) was added to a suspension of $[ReOCl_3(OPPh_3)(SMe_2)]$ (0.12 g, 0.18 mmol) in toluene (30 mL). The preceding general procedure gave 0.044 g (45%) of green crystals. ^{1}H NMR ($CDCl_3$, 360 MHz, ppm): δ 1.83 (s, 3H, CH_3), 2.43 (s, 3H, CH_3), 2.71 (s, 3H, CH_3), 2.90 (s, 3H, CH_3), 4.86 (d, $^3J_{H-H}$ = 8.0 Hz, 1H, Ar), 5.25 (s, 1H, C*H*), 5.92 (s, 1H, C*H*), 6.75 (d, $^3J_{H-H}$ = 7.7 Hz, 1H, Ar), 6.93 (m, 2H, Ar), 7.05 (m, 1H, Ar), 7.25 (m, 2H, Ar), 7.32 (dt, $^3J_{H-H}$ = 7.6, 1.6 Hz, 1H, Ar), 7.48 (dt, $^3J_{H-H}$ = 7.8, 1.6 Hz, 1H, Ar), 7.68 (d, $^3J_{H-H}$ = 7.9 Hz, 1H, Ar). IR (KBr, cm^{-1}): 1582, 1510, 1486, 1384, 1262, 944, 940, 766. MS (EI, *m*/*z* (%)): 586 (100) [M^+]. Anal. Calcd for $C_{22}H_{24}ClN_2O_3Re$: C, 45.10; H, 4.13; N, 4.78. Found: C, 44.8; H, 4.07; N, 4.50.

[ReOBr(DiPO)$_2$] (5). A solution of DiPOLi (0.054 g, 0.20 mmol) in toluene (20 mL) was added to a suspension of $[ReOBr_3(OPPh_3)(SMe_2)]$ (0.080 g, 0.10 mmol) in toluene (30 mL). The preceding general procedure gave 0.065 g (81%) of green crystals. ^{1}H NMR ($CDCl_3$, 360 MHz, ppm): δ 1.11, 1.31 (2 m, 24H, CH_3), 1.97 (s, 3H, CH_3), 2.26 (s, 3H, CH_3), 2.45 (s, 3H, CH_3), 2.64 (h, $^3J_{H-H}$ = 6.9 Hz, 1H, C*H*), 2.78 (s, 3H, CH_3), 3.30 (h, $^3J_{H-H}$ = 6.8 Hz, 1H, C*H*), 3.60 (h, $^3J_{H-H}$ = 6.7 Hz, 1H, C*H*), 3.99 (h, $^3J_{H-H}$ = 6.7 Hz, 1H, C*H*), 5.39 (s, 1H, C*H*), 5.68 (s, 1H, C*H*), 7.18 (m, 6H, Ar). IR (KBr, cm^{-1}): 1514, 1372, 1258, 1016, 972, 936, 798. MS (EI, *m*/*z* (%)): 799 (9) [M^+]. Anal. Calcd for $C_{34}H_{48}BrN_2O_3Re$: C, 51.1; H, 6.06; N, 3.51. Found: C, 51.5; H, 6.20; N, 3.46.

[ReOBr(DPO)$_2$] (6). A solution of DPOLi (0.040 g, 0.19 mmol) in toluene (20 mL) was added to a suspension of $[ReOBr_3(OPPh_3)(SMe_2)]$ (0.077 g, 0.098 mmol) in toluene (30 mL). The preceding general procedure gave 0.050 g (76%) of green crystals. ^{1}H NMR ($CDCl_3$, 360 MHz, ppm): δ 1.88 (s, 3H, CH_3), 2.02 (s, 3H, CH_3), 2.11 (s, 3H, CH_3), 2.30 (s, 3H, CH_3), 2.33 (s, 3H, CH_3), 2.42 (s, 3H, CH_3), 2.47 (s, 3H, CH_3), 2.73 (s, 3H, CH_3), 5.31 (s, 1H, C*H*), 5.85 (s, 1H, C*H*), 7.04 (m, 6H, Ar). IR (KBr, cm^{-1}): 1566, 1496, 1370, 1270, 966, 932, 766. MS (EI, *m*/*z* (%)): 686 (9) [M^+]. Anal. Calcd for $C_{26}H_{32}BrN_2O_3Re$: C, 45.5; H, 4.70; N, 4.08. Found: C, 45.5; H, 4.67; N, 4.03.

[ReOBr(APO)$_2$] (7). A solution of APOLi (0.038 g, 0.21 mmol) in toluene (20 mL) was added to a suspension of $[ReOBr_3(OPPh_3)(SMe_2)]$ (0.086 g, 0.11 mmol) in toluene (30 mL). The preceding general procedure gave 0.027 g (41%) of green crystals. ^{1}H NMR ($CDCl_3$, 360 MHz, ppm): δ 1.80 (s, 3H, CH_3), 2.42 (s, 3H, CH_3), 2.70 (s, 3H, CH_3), 2.90 (s, 3H, CH_3), 4.80 (d, $^3J_{H-H}$ = 8.0 Hz, 1H, Ar), 5.24 (s, 1H, C*H*), 5.92 (s, 1H, C*H*), 6.72 (d, $^3J_{H-H}$ = 7.4 Hz, 1H, Ar), 6.88 (m, 2H, Ar), 7.03 (m, 1H, Ar), 7.25 (m, 2H, Ar), 7.31 (m, 1H, Ar), 7.47 (m, 1H, Ar), 7.76 (d, $^3J_{H-H}$ = 8.0 Hz, 1H, Ar). IR (KBr, cm^{-1}): 1572, 1518, 1486, 1382, 1266, 1018, 970, 938, 764, 704, 704, 540. MS (EI, *m*/*z* (%)): 630 (7) [M^+]. Anal. Calcd for $C_{22}H_{24}BrN_2O_3Re \cdot C_7H_{16}$: C, 47.7; H, 5.52; N, 3.83. Found: C, 48.1; H, 5.28; N, 3.58.

Catalytic Epoxidation Reaction. The reactions were carried out under an inert atmosphere. A solution of *cis*-cyclooctene (0.30 g, 2.72 mmol), dibutyl ether (0.30 g, 2.30 mmol), and the respective rhenium(V) catalyst (2 mol %) were dissolved in chloroform (20 mL). The reaction mixture was heated to 50 °C, whereupon TBHP (1.5 mL, 5.5 M solution in decane, 8.2 mmol) was added. For GCMS analyses 1 mL samples were taken every 1 h. The reaction was quenched by addition of a small amount of MnO_2 to decompose excess TBHP and analyzed by GCMS.

Acknowledgment. We are grateful to the Deutsche Forschungsgemeinschaft for generous support of this work (MO 963/2).

Supporting Information Available: CIF files giving crystallographic data for *cis*-*N*,*N*-**2**, *cis*-*N*,*N*-**3**, *trans*-*N*,*N*-**3**, *cis*-*N*,*N*-**7** monoclinic, and *cis*-*N*,*N*-**7** triclinic. This material is available free of charge via the Internet at http://pubs.acs.org.