Bidentate Lewis Base Adducts of Methyltrioxorhenium(VII) and Their Application in Catalytic Epoxidation

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Received June 8, 2001

Methyltrioxorhenium(VII) (MTO) forms octahedral adducts with bidentate Lewis bases. These complexes were isolated and fully characterized, including X-ray crystallography. The compounds display distorted octahedral geometry in the solid state with a tendency of disorder concerning the Re central atom. At elevated temperatures, they undergo rapid ligand-exchange reactions in solution. The ease of this ligand exchange depends mainly on the Lewis basicity of the ligand. The more Lewis basic the ligand is, the stronger the metal−ligand interaction is, as can be shown by NMR spectroscopy. All examined complexes are temperature stable but quite sensitive to light and moisture. In the presence of H_2O_2, the complexes form very active and highly selective epoxidation catalysts. Peroxo complexes are generated, and at least one of the Re−N interactions is cleaved during this process. Total ligand dissociation only occurs in the case of very weakly coordinating bidentate ligands. The peroxo complexes of the MTO Lewis base adducts are, in general, more sensitive to water than MTO itself.

Introduction

The oxidation of organic compounds and the transformation of stoichiometric reactions into catalytic processes were under active investigation for several decades. Whereas industrial transformations of olefins into epoxides commonly involve the use of catalysts associated with either oxygen, hydrogen peroxide, or organic peroxides, stoichiometric oxidants are still commonly used mainly for the oxidation of fine chemicals.[1] The catalytic epoxidations applied in industrial processes usually utilize alkyl hydroperoxides as oxidizing agents.[2] An important improvement in the field of catalytic oxidation arose with the discovery by Herrmann and co-workers in 1991 of the catalytic activity of methyltrioxorhenium(VII) (MTO). This compound has emerged as one of the most active catalysts for olefin epoxidation in the presence of H_2O_2 as the oxidizing agent.[3] Since then, a large volume of research has been directed toward the investigation of the catalytic capabilities of MTO including the characterization and isolation of the catalytically active species,[4] the investigation of the reaction mechanism by experimental techniques and theoretical calculations, the effects of variation of the substituted olefins, and the modification of the catalytic reaction conditions.[5] Due to the Lewis acidity of the rhenium center, a significant drawback of this system is the concomitant cleavage of the epoxide ring leading to the formation of diols in the presence of water.[6] Several methods have been suggested during recent years to overcome this problem.[5,7] A very interesting approach to limit the deleterious side reactions is the use of Lewis bases as additives to the biphasic (H_2O_2/organic solvent) catalytic system.[7a] Lewis base adducts of MTO were first mentioned in 1989 by Herrmann et al.[8,9] Despite the positive effects of Lewis bases in enhancing the selectivity toward epoxides in the MTO-catalyzed olefin epoxidation, it was originally assumed that at least some Lewis bases would significantly reduce the activity of the catalytic system by reducing the Lewis acidity of the Re(VII) center.[7] A re-examination of these findings by Sharpless et al. showed that in the case of aromatic monodentate Lewis base adducts, such

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10.1021/ic010610f CCC: $20.00
Published on Web 09/14/2001

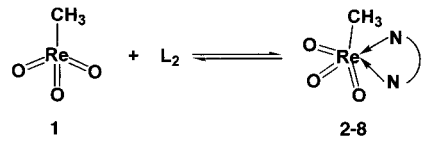
as pyridine, a mixture of MTO and excess Lewis base not only helps to avoid diol formation but also accelerates the olefin epoxidation, even in comparison to MTO itself.[10] Additionally, it was found that the use of 3-cyanopyridine and pyrazole as the Lewis base is more effective and less problematic than the use of pyridine,[10c,11] since the latter ligand can be easily oxidized to its *N*-oxide.[11] The pyridine *N*-oxide forms a highly selective though less active cocatalyst with MTO/H_2O_2. Conversely, it has been reported that bipyridine *N*,*N*′-dioxide is an effective species with respect to reducing the acidity of the catalytic system, suppressing the diol formation. It has been assumed that 2,2′-bipyridine is easily oxidized to its *N*-oxide by the MTO/H_2O_2 system, especially in the presence of olefins which are not so readily transformed to the corresponding epoxides.[12]

The multitude of results mentioned above might lead to the assumption that Lewis base adducts of methyltrioxorhenium(VII) and their *N*-oxide congeners are well-examined and fully characterized materials. However, a more careful study of the literature shows that the contrary is the case. Monodentate Lewis base adducts of MTO have only recently been examined in detail.[13] Bidentate Lewis base adducts have been mainly examined in situ to better understand their fluxional behavior. 4,4′-Di-*tert*-butyl-2,2′-bipyridine is the only bidentate Lewis base which has been studied in more detail with respect to its MTO adduct. The reaction chemistry of the latter complex surprisingly resembles in its reactivity the electron-rich and catalytically inactive pentamethylcyclopentadienyl trioxorhenium(VII).[14] No crystal structure of a bidentate MTO Lewis base adduct has been reported to date, and the original descriptions published on bidentate Lewis base adducts show that at least in some cases only the decomposition products, consisting of a protonated ligand and a perrhenate ion (ReO_4^-), were isolated and erroneously ascribed to the desired complexes.[8a,b] Considering the important applications of the title compounds, we characterized selected bidentate MTO complexes properly and reexamined the catalytic behavior on the basis of a sufficient characterization of the catalyst precursors in this work.

Experimental Section

All preparations and manipulations were carried out under an oxygen- and water-free argon atmosphere using the standard Schlenk techniques. Solvents were dried by standard procedures, were distilled, and were kept under argon over molecular sieves. The ligands were bought from Aldrich and Lancaster, with the exception of 4,4′-di-*tert*-butyl-2,2′-bipyridine which was prepared according to the procedure described in the literature.[15] Elemental analyses were performed in the Mikroanalytisches Labor of the TU München in Garching. ^{1}H, ^{13}C, and ^{17}O NMR were measured in deuterated solvents (Deutero GmbH, Aldrich) in a Bruker DPX 400 spectrometer. IR spectra were recorded on a Perkin-Elmer FTIR spectrometer using KBr pellets as the IR matrix. Raman measurements were carried out using a Bio-Rad 575C FTS Raman spectrometer. The H_2O_2 was gradually added to a CH_2Cl_2 solution of the complexes, and spectra were collected both in organic and in aqueous phase.

Preparation of complexes $ReO_3(CH_3)$(LL) (LL = 2,2′-bipyridine, **2**; 4,4′-dimethyl-2,2′-bipyridine, **3**; 4,4′-di-*tert*-butyl-2,2′-bipyridine, **4**; 1,10-phenanthroline, **5**; 4,7-dimethyl-1,10-phenanthroline, **6**; 4,7-diphenyl-1,10-phenanthroline, **7**; and 2,2′-bipyrimidine, **8**) were made following a similar synthetic procedure reported in the literature for complex **2**,[16b] that is, by reaction of MTO (**1**) with the corresponding ligand in a 1:1 molar ratio in THF at room temperature (eq 1).



1 **2-8** (1)

L_2 = 2,2'-bipyridine (**2**)
4,4'-dimethyl-2,2'-bipyridine (**3**)
4,4'-bis(t-butyl)-2,2'-bipyridine (**4**)
1,10-phenanthroline (**5**)
4,7-dimethyl-1,10-phenanthroline (**6**)
4,7-diphenyl-1,10-phenanthroline (**7**)
2,2'-bipyrimidine (**8**)

Methyl(2,2′-bipyridine)trioxorhenium (2).[16] Anal. Calcd for $C_{11}H_{11}N_2O_3Re$ (405.4): C, 32.59; H, 2.73; N, 6.91. Found: C, 32.42; H, 2.60; N, 6.84. ^{1}H NMR (400 MHz, $CDCl_3$, room temperature): δ 1.63 ($ReCH_3$, s, 3), 7.48 (py-H, t, 2), 8.01 (py-H, q, 2), 8.32 (py-H, d, 2), 8.94 (py-H, d, 2). ^{13}C{^{1}H} NMR (100.51 MHz, $CDCl_3$, room temperature): δ 25.6 ($ReCH_3$), 122.3, 125.4, 138.6, 149.6 (py-C). Selected IR (KBr): ν = 3108 w, 3080 w, 1600 m, 1443 m, 1317 m, 1156 m, 1032 m, 935 vs, 908 vs, 855 vs, 777 s, 735 m.

Methyl(4,4′-dimethyl-2,2′-bipyridine)trioxorhenium (3). Anal. Calcd for $C_{13}H_{15}N_2O_3Re$ (433.4): C, 36.02; H, 3.49; N, 6.46. Found: C, 36.53; H, 3.20; N, 6.45. ^{1}H NMR (400 MHz, $CDCl_3$, room temperature): δ 1.20 ($ReCH_3$, s, 3), 2.53 ($C_5H_3N-CH_3$), 7.33 (py-H, d, 2), 8.08 (py-H, s, 2), 8.86 (py-H, d, 2). ^{13}C{^{1}H} NMR (100.51 MHz, $CDCl_3$, room temperature): δ 25.9 ($ReCH_3$), 21.5 (py-CH_3), 123.5, 124.6, 126.9, 149.1, 151.3 (py-C). Selected IR (KBr): ν = 2964 w, 1615 s, 1488 m, 1407 m, 1030 m, 938 vs, 913 vs, 849 vs, 836 vs.

Methyl(4,4′-di-*tert*-butyl-2,2′-bipyridine)trioxorhenium (4). Anal. Calcd for $C_{19}H_{27}N_2O_3Re$ (517.6): C, 44.09; H, 5.26; N, 5.41. Found: C, 43.97; H, 5.30; N, 5.33. ^{1}H NMR (400 MHz, $CDCl_3$, room temperature): δ 1.09 (ReCH3, s, 3), 1.43 (C(CH3)3, s, 18), 7.53 (py-H, dd, 2), 8.18 (py-H, d, 2), 8.94 (py-H, d, 2). ^{13}C{^{1}H} NMR (100.51 MHz, $CDCl_3$, room temperature): δ 26.9 ($ReCH_3$), 30.4 ($C(CH_3)_3$), 35.6 ($C(CH_3)_3$), 119.6, 123.6, 149.3, 150.8, 164.4 (py-C). Selected IR (KBr): ν = 2964 m, 1617 m, 1413 m, 1254 m, 938 vs, 915 vs, 853 vs.

Methyl(1,10-phenanthroline)trioxorhenium (5). Anal. Calcd for $C_{13}H_{11}N_2O_3Re$ (429.6): C, 36.35; H, 2.56; N, 6.52. Found: C, 36.33; H, 2.48; N, 6.47. ^{1}H NMR (400 MHz, $CDCl_3$, room temperature): δ 1.07 ($ReCH_3$, s, 3), 7.91 (phen-H, t, 2), 8.06 (phen-H, s, 2), 8.57 (phen-H, d, 2), 9.37 (phen-H, d, 2). ^{13}C{^{1}H} NMR (100.51 MHz, $CDCl_3$, room temperature): δ 28.0 ($ReCH_3$), 125.9, 128.1, 131.5, 139.1, 142.5, 149.7 (phen-C). Selected IR (KBr): ν = 3058 m, 2998 m, 1626 m, 1582 m, 1517 s, 1426 s, 1221 m, 939 vs, 919 vs, 905 vs, 873 s, 846 vs, 727 vs, 648 m.

Methyl(4,7-dimethyl-1,10-phenanthroline)trioxorhenium (6). Anal. Calcd for $C_{15}H_{15}N_2O_3Re$ (457.6): C, 39.38; H, 3.30; N, 6.12. Found: C, 40.04; H, 3.80; N, 5.75. ^{1}H NMR (400 MHz, $CDCl_3$, room temperature): δ 0.91 ($ReCH_3$, s, 3), 2.91 (phen-CH_3, s, 6), 7.71 (phen-H, s, 2), 8.20 (phen-H, s, 2), 9.23 (phen-H, s, 2). ^{13}C{^{1}H} NMR (100.51 MHz, $CDCl_3$, room temperature): δ 19.7 (phen-CH_3), 28.1 ($ReCH_3$), 121.6, 158.1, 162.1 (phen-C). Selected IR (KBr): ν = 3083 w, 2973

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Table 1. Summary of Data for Crystal Structure Analysis of Compound **5**

	5
empirical formula	$C_{13}H_{11}N_2O_3Re$
fw	429.45
crystal system	monoclinic
space group	$P2_1/n$ (No. 14)
a, Å	8.6152(1)
b, Å	11.6056(2)
c, Å	12.7074(2)
β, deg	106.2269(7)
V, Å^3	1219.93(3)
Z	4
μ , mm^{-1}	9.966
λ, Å	0.71073
T, K	173
no. reflections collected	21079
no. independent reflections/(R_{int})	2794/0.037
no. observed reflections [$I > 2\sigma(I)$]	2693
R1[a], wR2 [b] indices[$I > 2\sigma(I)$]	0.0189, 0.0439
R1, wR2 indices (all data)	0.0201, 0.0443
GOF[c]	1.108

[a] $R1 = \sum(||F_o| - |F_c||)/\sum|F_o|$. [b] $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$. [c] $GOF = [\sum w(F_o^2 - F_c^2)^2/(NO - NV)]^{1/2}$.

w, 1622 m, 1578 m, 1521 s, 1428 s, 1235 m, 941 vs, 920 vs, 904 vs, 868 s, 844 vs, 730 m.

Methyl(4,7-diphenyl-1,10-phenanthroline)trioxorhenium (7). Anal. Calcd for $C_{25}H_{19}N_2O_3Re$ (581.6): C, 51.63; H, 3.29; N, 4.82. Found: C, 51.27; H, 3.70; N, 4.67. ^{1}H NMR (400 MHz, $CDCl_3$, room temperature): δ 1.08 ($ReCH_3$, s, 3), 7.54 (phenyl-H, s, 4), 7.58 (phenyl-H, s, 6), 7.85 (phen-H, s, 2), 8.07 (phen-H, s, 2), 9.42 (phen-H, s, 2). ^{13}C{^{1}H} NMR (100.51 MHz, $CDCl_3$, room temperature): δ 27.9 ($ReCH_3$), 125.6, 129.2, 129.5, 129.8, 135.7, 142.1, 148.5, 151.8 (phenyl- and phen-H). Selected IR (KBr): ν = 3054 w, 2969 w, 1621 m, 1597 m, 1560 m, 1518 s, 1493 m, 1422 s, 1395 m, 1263 m, 1232 m, 1062 m, 942 vs, 919 vs, 903 s, 851 vs, 838 vs, 802 m, 765 m, 738 s, 702 vs, 633 m.

Methyl(2,2′-bipyrimidine)trioxorhenium (8). Anal. Calcd for $C_9H_9N_4O_3Re$ (407.2): C, 26.53; H, 2.23; N, 13.75. Found: C, 27.16; H, 2.10; N, 14.03. ^{1}H NMR (400 MHz, $CDCl_3$, room temperature): δ 2.50 ($ReCH_3$, s, 3), 7.43 (N(CH)(C*H*), s, 2), 9.02 (N(C*H*), s, 4). ^{13}C{^{1}H} NMR (100.51 MHz, $CDCl_3$, room temperature): δ 19.2 ($ReCH_3$), 123.6, 126.0, 148.6 (pyrimidine-C). Selected IR (KBr): ν = 3069 w, 3043 w, 1574 s, 1552 s, 1404 vs, 941 vs, 916 vs, 853 s, 833 m, 761 m, 659 m.

X-ray Structure Determination of Complex 5. Details of the X-ray experiment, data reduction, and final structure refinement calculation are summarized in Table 1. Crystals of complex **5** suitable for X-ray structure determination were grown by slow evaporation of a saturated solution of **5** in a mixture of diethyl ether and dichloromethane. Preliminary examination and data collection were carried out on a Nonius Kappa CCD area detector at the window of a rotating anode X-ray generator (NONIUS FR591, 50 kV, 80 mA, 4.0 kW) and graphite monochromated Mo Kα radiation (λ = 0.71073 Å). Data collection were performed at 173 K with an exposure time of 20 s per film (φ- and Ω-scan, rotation modus, $\Delta\varphi/\Delta\Omega = 2.0°$) and were controlled by the Collect software package.[17a] Collected images were processed using Denzo. The unit cell parameters were obtained by full-matrix least-squares refinements of 2914 reflections.[17b] The structure was solved by a combination of direct methods and difference Fourier syntheses.[17c] All non-hydrogen atoms of the asymmetric unit were refined with anisotropic thermal displacement parameters. All hydrogen atoms were found in the difference Fourier map and were refined freely with individual isotropic thermal displacement parameters. Full-matrix least-squares refinements were carried out by minimizing $\sum w(F_o^2 - F_c^2)^2$ with the SHELXL-97 weighting scheme and were stopped at maximum shift/err < 0.001.[17d] Neutral atom scattering factors for all of the atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from *International Tables for Crystallography*.[17e] All of the other calculations (including ORTEP graphics) were done with the program PLATON.[17f] Calculations were performed on a PC workstation (Intel Pentium II) running LINUX.

Catalysis Reactions with Compounds 1−8 as Catalysts. *cis*-Cyclooctene (400 mg, 3.65 mmol) and *n*-dibutyl ether (400 mg, internal standard), 1 mol % (36 μmol) **1**−**8** (as catalyst), an appropriate amount of ligand, and 2.5 mL of $CH_2Cl_2/CHCl_3$ were added to a thermostated reaction vessel. Hydrogen peroxide (0.8 mL, 35%, 9.3 mmol) was added to start the reaction. The two-phase reaction system was stirred for 24 h. The course of the reaction was monitored by quantitative GC analysis; samples were taken from the organic phase, were diluted with CH_2Cl_2, and were treated with a catalytic amount of MnO_2 and $MgSO_4$ to destroy the hydrogen peroxide and to remove the water. The resulting slurry was filtered over a filter equipped with a Pasteur pipet, and the filtrate was injected into a GC column. The conversion of *cis*-cyclooctene and the yield of cyclooctene epoxide were calculated from a calibration curve (r^2 = 0.999) recorded prior to the reaction course.

Results and Discussion

Synthesis and Spectroscopic Examinations of Compounds 2−8. The reaction of MTO with bidentate Lewis bases in THF at room temperature results in the formation of yellow-colored compounds of the type CH_3ReO_3(LL) as presented in eq 1. Complex **8** is soluble in CH_2Cl_2, $CHCl_3$, and THF; **4**, **6**, and **7** are soluble in CH_2Cl_2 and $CHCl_3$; and **3** and **5** are soluble in CH_2Cl_2 and only moderately soluble in $CHCl_3$. The complexes are thermally stable both in the solid and in the solution states under an inert gas atmosphere which is in contrast to some of the monodentate Lewis base derivatives of MTO which were found to decompose at room temperature (e.g., methyl(pyridine)-trioxorhenium).[13a] In the solid state, the complexes are stable in air for a few hours, but they are somewhat sensitive to light and decompose to black residues containing polymeric ReO_3.

In the IR spectra of complexes **2**−**8**, the symmetric Re═O stretching vibrations appear within a narrow interval (935−942 cm^{-1}), and the asymmetric stretching vibrations occur between 908 and 920 cm^{-1} (see Table 2). The corresponding force constants f(Re═O) can be derived from the ν(Re═O) values.[16] Complexes **2**−**8** exhibit Re═O force constants ranging between 7.42 and 7.57 m dyn Å^{-1} which are much lower than that of **1** (8.46 m dyn Å^{-1}), reflecting that additional electron density donated from the Lewis base ligand to the Re(VII) center significantly weakens the Re═O bonds. However, this weakening is not reflected to a significant extent in the X-ray crystal structures (see below). The ν(Re═O) bands of compounds **2**−**8** are too close, especially with respect to the error range of the IR spectrometer (±2 cm^{-1}), to allow a discussion with respect to the influence of the particular ligands LL used. The Re═O bond weakening caused by the bidentate ligands is comparable to that caused by monodentate Lewis bases.[13a]

Interestingly, the ^{1}H and ^{13}C NMR data of the Re−CH_3 group (Table 2) clearly reflect the electron-donating capability of the ligands. The weaker the donor ability of the Lewis base, the closer, in general, are the observed δ(^{1}H) and δ(^{13}C) values to that of **1** with respect to its NMR data. It is possible to correlate

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Table 2. Selected IR (KBr), ^{1}H, ^{13}C, and ^{17}O NMR (in $CDCl_3$) Data, Calculated Force Constants *f*(ReO), and pK_a of the Ligands

	ν(Re═O)/cm^{-1}		$ReCH_3$				pK_a of L	
compound	ν_s	ν_{as}	$\delta(^1H)$	$\delta(^{13}C)$	ReO_3 $\delta(^{17}O)$	*f*(Re═O) mdyn Å^{-1}	ref 18	ref 19
1	999	957	2.67	19.0	829[a]	8.46		
2	935	908	1.63	25.6	722 (170), 649 (400)[c]	7.42	4.3	3.62
3	938	913	1.20	25.9	740 (900)[a] 724 (800), 652 (1100)[b] 719 (250), 648 (650)[c]	7.48		4.40
4	938	915	1.09	26.9	729 (1350)[a] 723 (500), 650 (900) 719 (300), 647 (700)[c]	7.49		n.k.
5	939	919	1.07	28.0	733 (900)[a] 731 (400), 655 (720)[b] 727 (200), 648 (500)[c]	7.53	5.2	4.53
6	941	920	0.91	28.1	726 (170), 556 (300)[a] 725 (220), 753 (480)[b] 722 (240), 647 (530)[c]	7.56		5.40
7	942	919	1.08	27.9	728 (250), 654 (600)[a] 726 (270), 650 (600)[b] 724 (370), 640 (810)[c]	7.57		4.30
8	941	916	2.50	19.2	824 (60)[a] 818 (75)[b] 778 (1070)[c]	7.54	0.6	

[a] 25 °C. [b] 0 °C. [c] −55 °C; n.k.−not known

the chemical shift of the CH_3 group with ligand basicity. The 2,2′-bipyrimidine ligand with four nitrogens (pK_a = 0.6) is considerably less basic than 2,2′-bipyridine and 1,10-phenantroline (pK_a = 4.3 and 5.2, respectively) and thus undergoes only a relatively weak interaction with the Re(VII) center.[18] The $\delta(^1H)$ of $ReCH_3$ of **2** is located at 1.63 ppm (pK_a = 3.62). This signal shifts upfield to 1.20 in **3** (pK_a = 4.4) and 1.09 ppm in **4** (to the best of our knowledge, the pK_a is not reported in the literature) due to the electron-donating nature of the methyl/*tert*-butyl substituents resulting in an increase of the donor ability of the alkyl-substituted 2,2′-bipyridines.[19] The $\delta(^1H)$ of $ReCH_3$ in the 1,10-phenanthroline adducts show signals that shift upfield in the order **7** ≥ **5** > **6** which is in good agreement with the published pK_a values.[19]

The ^{17}O NMR spectroscopy shows analogous correlations. The Lewis base ligands donate electron density to the Re(VII) center, thereby increasing the electron density of the terminal oxygens and resulting in $\delta(^{17}O)$ resonances at lower field compared to MTO. Compound **8** once again exhibits the closest resemblance to **1** due to the weak donor ability of 2,2′-bipyrimidine. The ^{17}O NMR spectra were measured at 25, 0, and −55 °C, respectively (see Table 2). At 0 and −55 °C, complexes **2**−**7** show two signals. A broad signal is located at ca. 720−730 ppm and stems from the axial oxygen ligands which are trans to the N atoms of the Lewis base. A smaller resonance appears in the 640−650 ppm region and is assigned to the oxo ligand trans to the methyl group. In the case of **2**−**5**, the equatorial and axial signals coalesce at room temperature and display very broad half-widths (greater than 900 Hz). This behavior can be explained by a quick oxygen-exchange process.[9] A comparable process also takes place in the case of **6** and **7** but at higher temperatures. A good donor ability of the rigid ligands obviously helps to maintain the rigid coordination sphere even at elevated temperatures.

The coordination of bidentate Lewis base ligands to MTO is governed not only by electronic but also by steric effects. The synthesis of a 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline MTO adduct was attempted under similar conditions, but only free ligand and MTO were obtained. This indicates that the methyl groups in position 2 and 9 of 1,10-phenantroline lead to an excessively bulky ligand which cannot coordinate to MTO.

Considering only the ^{17}O NMR data, it is not clear whether the signal coalescence at higher temperatures is due to a ligand-exchange phenomenon or due to an internal ligand rotation. The question of whether an intramolecular or an intermolecular process occurs was settled by ^{1}H NMR spectroscopic analysis. When a solution of **4** in $CDCl_3$ is treated with 1 equiv of 4,4′-*tert*-butyl-2,2′-bipyridine at 25 °C, neither the original resonance of the adduct **4** nor the resonances from the free ligand are found. Instead, fully averaged signals were observed at δ = 0.97 (s, 3H, $ReCH_3$), 1.40 (s, 36H, $C(CH_3)_3$), 7.42 (s, 4H, py-H), 8.28 (s, 4H, py-H), and 8.78 (s, 4H, py-H). Cooling the solution to −55 °C leads to discrimination of the signals due to **4** and to the free ligand. This observation suggests a ligand-exchange process. The equilibrium shown in eq 1 is rapid relative to the NMR time scale at room temperature. This exchange behavior was also observed in the monodentate Lewis base adducts of MTO,[13,20,21] but it does not appear to be prominent in the case of Mo(VI) complexes of the type MoO_2X_2L (X = Cl, Br) and MoO_2R_2L (R = CH_3, C_2H_5).[22] If 1 equiv of 4,7-dimethyl-1,10-phenanthroline is mixed with complex **4** in $CDCl_3$ at 25 °C, a Lewis base ligand exchange takes place immediately. In our experiment, we did not observe complex **4** and free ligand 4,7-dimethyl-1,10-phenanthroline, but rather we observed complex **6** and free ligand 4,4′-*tert*-butyl-2,2′-bipyridine. This can be explained on the basis of the relative donating abilities of 4,7-dimethyl-1,10-phenanthroline and 4,4′-*tert*-butyl-2,2′-bipyridine. Raising the temperature to 55 °C did not produce any obvious changes in the ^{1}H NMR spectrum. However, cooling the solution to −55 °C led to a mixture of about 45% of **6**, 45% of 4,4′-*tert*-butyl-2,2′-bipyridine free ligand, 5% of **4**, and 5% of 4,7-dimethyl-1,10-phenanthroline free ligand. This result is in accord with the donor capabilities of the ligands used (see Table 2).

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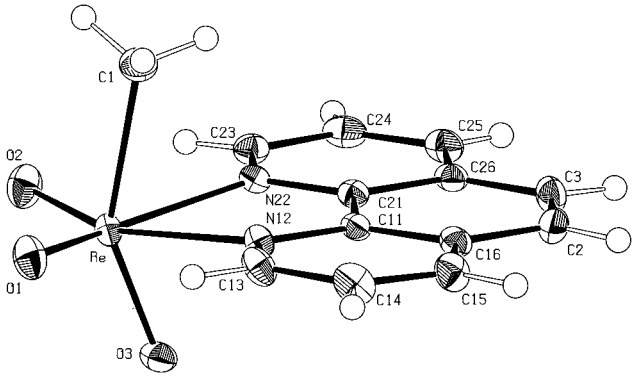

Figure 1. PLATON[17f] drawing of complex **5** in the solid state. Thermal ellipsoids are at the 50% probability level.

Table 3. Selected Interatomic Distances (Å) and Angles (deg) for Compound **5**

Re−O1	1.717(2)	Re−N12	2.291(2)
Re−O2	1.718(3)	Re−N22	2.298(2)
Re−O3	1.767(3)	Re−C1	2.199(4)
O1−Re−O2	107.08(12)	O2−Re−C1	92.23(14)
O1−Re−O3	105.32(12)	O3−Re−N12	80.18(10)
O1−Re−N12	89.72(10)	O3−Re−N22	78.54(10)
O1−Re−N22	160.40(10)	O3−Re−C1	149.63(13)
O1−Re−C1	91.66(13)	N12−Re−N22	71.81(9)
O2−Re−O3	106.08(12)	N12−Re−C1	74.82(13)
O2−Re−N12	159.26(10)	N22−Re−C1	77.48(11)
O2−Re−N22	89.80(10)		

Crystal Structure Examinations. The crystal structures of complexes **2**, **3**, and **5** were examined. However, the structures of compounds **2** and **3** are disordered with respect to the position of the metal center. The metal center is found either above or below the equatorial plane. This behavior does not allow a reliable determination of the bond distances and the bond angles in these two molecules. The crystal structure of compound **5** involves discrete molecules without any short interatomic contacts. The molecular structure of compound **5** in the solid state is shown in Figure 1, and selected bond lengths and angles are listed in Table 3. Complex **5** displays a distorted octahedral geometry[23] 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. The same arrangement is found for complexes **2** and **3**. The Re═O bond distances in the case of complex **5** of 1.717(2) and 1.718(3) Å are very similar to those of all known Re(VII) oxo complexes containing an Re═O double bond.[20] The Re−N bond distances are comparatively long, 2.291(2) and 2.298(2) Å, indicating a weak N→Re bonding interaction and, therefore, supporting the spectroscopic results given before.

Distances and angles within the Lewis base ligand are unexceptional and do not require further comment. Similar observations with respect to the coordinating Lewis base ligands have been made for Mo(VI) oxo complexes.[24]

Epoxidation Catalysis. MTO reacts with H_2O_2 to form an isolable bisperoxo complex via a monoperoxo intermediate.[25,26] It is believed that both the mono- and bisperoxo species are active catalysts depending on the reaction conditions.[25] The aims of our study were to evaluate how the catalytic performance with respect to time is affected by the following: (a) the use of different bidentate Lewis base adducts of MTO, (b) the ligand amount, (c) the use of noncoordinating solvents with different polarity, (d) temperature, and (e) competing oxidation reactions between the olefin and the Lewis base present.

Effects of the Type and Amount of Lewis Base. The catalytic performances of the different MTO adducts in $CHCl_3$ and CH_2Cl_2 were evaluated at 30 °C. With $CHCl_3$ as the solvent, the yield of cyclooctene epoxide is relatively low for complexes **2**−**7** (see Figure 2a). Complex **8** gives a much higher catalytic yield (ca. 72%) (Figure 2a). The use of excess ligand (1:3 and 1:5, MTO:ligand ratios) results in a considerable increase of the epoxide yields in the case of complexes **2**−**7**. The reason for the observed different behavior of complexes **2**−**7** and **8** is probably the quite weak coordination ability of 2,2′-bipyrimidine. As indicated by both Raman and NMR examinations, the 2,2′-bipyrimidine ligand is completely lost after the addition of H_2O_2 and does not contribute to the stabilization of the active species (see below). However, due to its higher basicity, the ligand contributes to a higher OH^- concentration in solution thus leading to an increased catalyst decomposition.[13b,21] This is most notable in the case of high concentrations of 2,2′-bipyrimidine, where significant amounts of ReO_4^- are found. For all ligands other than 2,2′-bipyrimidine, the epoxide yield increases with increasing ligand excess. A 5-fold excess is sufficient to obtain maximum epoxide yields and conversions; the turnover frequencies (TOF) increase is usually proportional to the ligand amount, and the selectivity is improved relative to pure MTO as the catalyst precursor. The solubility of the different adducts of MTO in $CHCl_3$ is quite low and is improved by addition of H_2O_2.

The use of CH_2Cl_2 as a solvent in the catalytic runs shows quite different results (see Figure 2b). A ligand amount dependence in this solvent is not observed. For all complexes **2**−**8**, we obtained the maximum values of epoxide yields, and they are similar to those obtained with a MTO:ligand ratio of 1:5 in $CHCl_3$. When the ligand amount was increased to a 3-, 5-, and 10-fold excess, the yield changes are, in general, negligible. Exceptions are adducts **6** and **8** which show low epoxide yields especially at a 10-fold excess of ligand.

Solvent Effects. Solvent effects in homogeneous catalysis were reported in the literature.[27,28] In this case, the solvent effect can be explained in the following manner: H_2O_2 exists in equilibrium with HO_2^- and H^+. The Lewis base present also behaves as a Brønsted base.[13b] The nature of the base will determine the concentration of HO_2^- ions. However, the existence of these ions as an ion pair or as free ions will be defined by the dielectric constant of the solvent. CH_2Cl_2 has a dielectric constant of 9.08 at 20 °C, much higher than that of $CHCl_3$ (4.81).[29] Therefore, CH_2Cl_2 will more readily accommodate the existence of free ions, resulting in a much more active system than that with $CHCl_3$. Consequently, even at a

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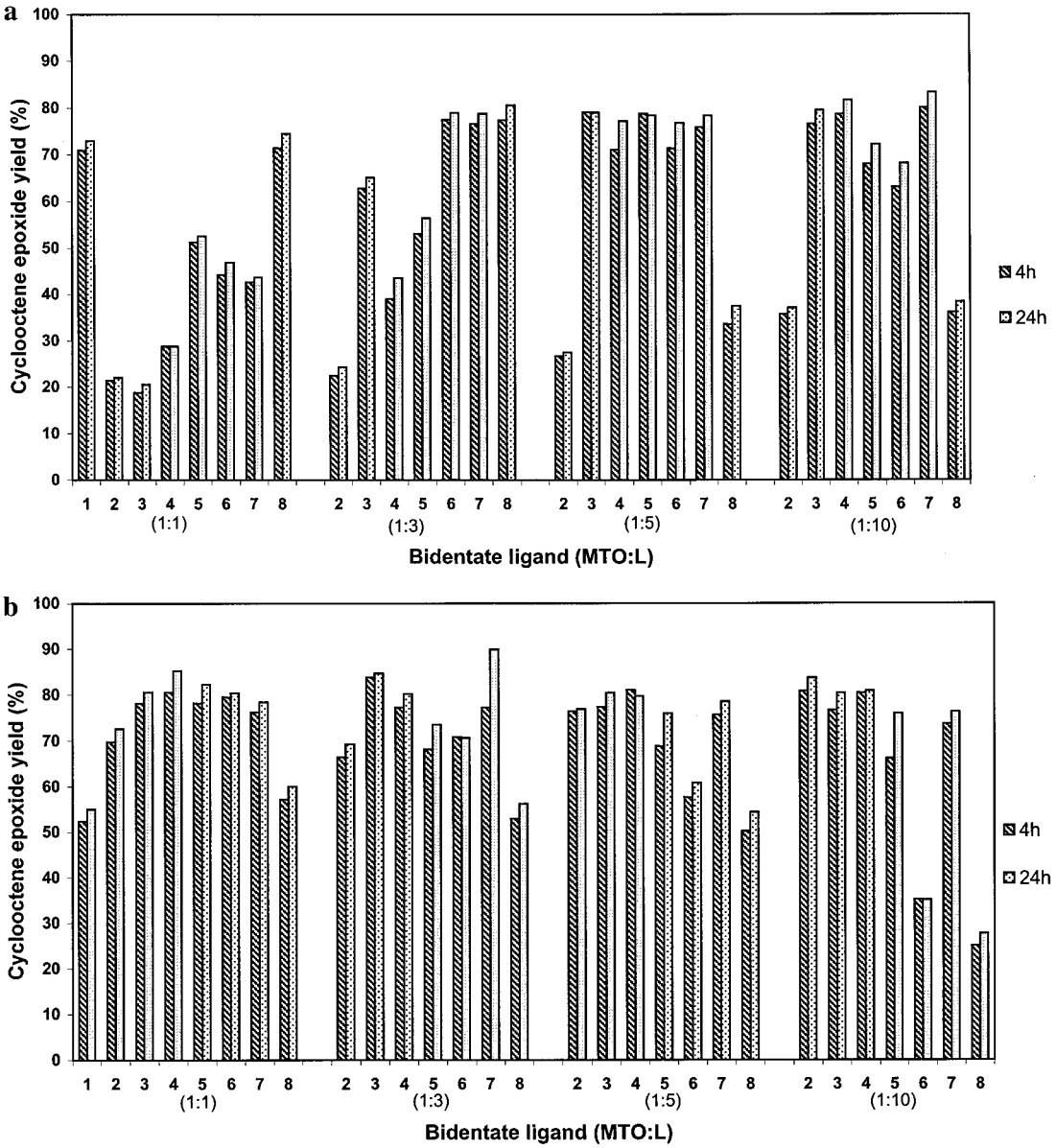

Figure 2. (a) Cyclooctene epoxide yields in $CHCl_3$. (b) Cyclooctene epoxide yields in CH_2Cl_2.

1:1 ratio of MTO to ligand in CH_2Cl_2, excellent epoxide yields are achieved. In $CHCl_3$, an excess of base is required to increase the HO_2^- concentration to accomplish a comparable activity due to the lower dielectric constant.

The turnover frequencies (determined after a 5-min reaction time) reached in CH_2Cl_2 were ca. 550 mol/(mol h) in the case of MTO:ligand = 1:1 (in $CHCl_3$ up to ca. 330 mol/(mol h)). The TOFs increased to ca. 700 mol/(mol h) in CH_2Cl_2 when 1:5 MTO:ligand ratios are applied (in $CHCl_3$, they reach ca. 440 mol/(mol h) with a MTO:ligand ratio of 1:10).

In the cases of complexes **2**−**8**, without an excess of the ligand, the catalytic reaction reaches almost the maximum yield after 4 h. Running the reaction for 24 h does not significantly improve the yield. Significant diol formation is not observed. All of the catalytic reactions show a similar time-dependence curve. The first hour sees a rapid increase of the yield, after which the reaction rate slows down, and the epoxide yield almost stabilizes. Addition of more catalyst to the catalytic system leads to a further increase of the epoxide yield, suggesting catalyst decomposition. This is clearly exemplified in Figure 3, where complex **4** is used as the catalyst. After 1 h, a maximum epoxide yield (ca. 27%) was reached. On addition of more catalyst (36 mmol), a new increase of epoxide yield occurs. After approximately 1 h, a new maximum is observed. A further addition of **4** leads once again to an improvement of the yield. No induction time is observable. An addition of more substrate after the first hour did not lead to an improvement of the catalytic yield, confirming that the concentration of epoxide stops increasing due to the catalyst decomposition and not due to the absence of *cis*-cyclooctene.

Temperature Effects. The temperature effect on the catalytic activity was evaluated for complexes **3**, **5**, and **8** in $CHCl_3$ (see Table 4). At 55 °C, the total yield after 4 h is significantly lower than that at 30 °C, regardless of whether the ligand was present in an equimolar or in a 5-fold excess. The yields at 0 °C are better than those at 30 °C for all of the complexes examined. However, the catalytic activities decrease with decreasing temperatures. Warming the reaction from −20 to 0 °C leads to an increase of the epoxide yield, which indicates that the low yields (at −20 °C) are not due to decomposition but due to a sluggish reaction at this temperature. A careful examination of the epoxide yield curves shows that the TOFs increase in the order of temperatures 0 < 30 < 55 °C (Table 4) and that the lifetimes of the catalysts decrease in the same order. Accord-

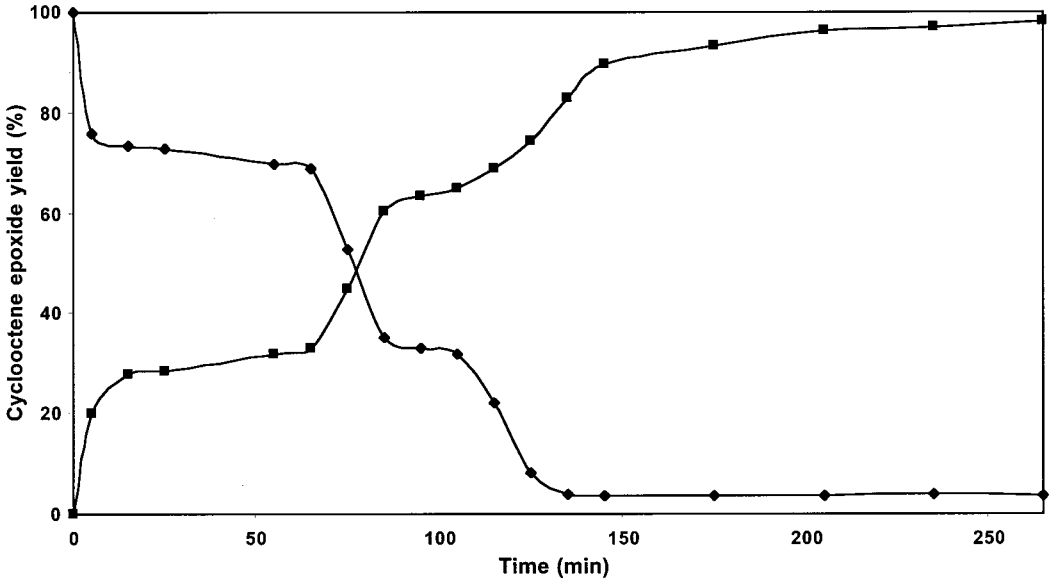

Figure 3. Reactivation of the catalytic activity by addition of more catalyst (compound **4**).

Table 4. Selected Time-Dependent Turnover Frequency Values Calculated after a 5-Min Reaction Time[a]

complex	0 °C	30 °C	55 °C
3	70	210	230
6	20	70	180
8	200	320	405

[a] The turnover frequency is defined as [mol of epoxide/[mol of catalyst·time (h)]].

ingly, at 0 °C, all three catalysts are active during the initial 4 h. At 30 °C, the lifetime decreases to approximately 1 h in the case of catalyst **3**, and ca. 2 h in the case of complexes **5** and **8**. The ligand−Re(VII) interaction is considerably weakened at higher temperatures.[9a] An evidence of this is the downfield shift of the resonance assigned to the protons of the CH_3 coordinated to Re, with increasing temperature, caused by the reduction of the electron density on the metal center. At 55 °C, the ligands are more likely to dissociate from MTO which in the absence of the coordinating Lewis bases is more easily decomposed to the perrhenenate ion and methanol due to the presence of higher OH^- concentrations.[13b,21]

Influence of the Presence of *N*-Oxides. A ^1H NMR of samples of the organic phase of a catalytic run in $CDCl_3$ does not show the presence of oxidized Lewis base. However, to test the activity of the *N,N*′-dioxide ligated complex, 2,2′-bipyridine-*N,N*′-dioxide and 4,4′-di-*tert*-butyl-2,2′-bipyridine-*N,N*′-dioxide were synthesized[30] and were used as additives in the MTO-catalyzed oxidation of *cis*-cyclooctene. The use of a 1:1 ratio of MTO to 2,2′-bipyridine-*N,N*′-dioxide in both solvents leads to a high conversion (ca. 96%) and to excellent selectivity (ca. 91%). However, with the use of a 1:5 ratio, the epoxide yield decreases to ca. 40% in CH_2Cl_2 and to 75% in $CHCl_3$. The TOFs are much lower in the case of the 5-fold excess of ligand. The 4,4′-di-*tert*-butyl-2,2′-bipyridine-*N,N*′-dioxide complex of MTO gives very poor yields (lower than 35%) due to the weak coordination of the ligand to MTO, its peroxo complexes, and its good solubility in the aqueous phase (water forms as a byproduct during the course of the epoxidation reaction). This behavior is very similar to that observed for monodentate pyridine *N*-oxides.[10c]

Raman Studies of the Catalytic Interactions. The interactions of complexes **4**, **6**, and **8** in CH_2Cl_2 solution with a 0.5−300-fold excess of H_2O_2 were additionally examined by Raman spectroscopy. The interactions of these complexes with a 0.5−2-fold excess of H_2O_2 were also followed by ^1H NMR spectroscopy.

Very small spectral changes can be observed on the addition of an equimolar amount of H_2O_2 to complexes **4** and **6**. Using a 2-fold excess of H_2O_2, these differences become more pronounced. The ligand bands shift to lower frequencies close to the stretching frequencies of the free ligand. Thus, coordination of the bidentate ligand must be altered due to the reaction with H_2O_2. The ligand may behave in a monodentate fashion with weak Re−N coordination.[31] Similar observations have been made in the case of $MoO(O_2)_2(LL)$ systems after the addition of *tert*-butyl hydroperoxide by Thiel et al.[32] However, the absence of vibrations of free MTO or ligand free mono- and bisperoxo complexes demonstrates that the ligand remains attached to the Re center. Bands belonging to a peroxo species formed on reaction with H_2O_2 can be observed (ν (cm^{-1}) = 1006 (sh), 887, 870, 831). A strong and broad IR band is observed at ca. 330 cm^{-1} that can be attributed either to the symmetric stretching $Re(O_2)$ vibration or to a Re−N stretching. The absence of free MTO or its peroxo complexes suggests that the ligand remains coordinated to Re during the experiment time.

Pronounced changes in the Raman spectra of complexes **4** and **6** are only observed when a large excess of H_2O_2 is added (at least 50-fold). In addition to the initial bands of complex **4** (bands at 943 and 910 cm^{-1} ν(Re═O), 354 and 334 cm^{-1} $\nu(ReN_2)$), new spectral features are observed. A weak band at 1017 cm^{-1} and another three bands at 871, 329, and 319 cm^{-1} appear. These bands belong to a peroxorhenium species. The latter two bands are presumably weakened ReN_2 bond vibrations and overlap with the $\nu(Re(O_2))$ stretching frequency. In the aqueous phase, bands due to the perrhenate ion, $[ReO_4]^-$, are found together with bands from the peroxo complexes.[33] No evidence of a free ligand in the organic phase was observed.

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Complex **8** exhibits a completely different behavior in comparison to complexes **4** and **6**. On addition of H_2O_2, only vibrational bands belonging to noncoordinating 2,2′-bipyrimidine and ligand-free MTO peroxo species appear in the IR and Raman spectra. ^1H and ^{17}O NMR examinations also only show signals of free 2,2′-bipyrimidine ligand and the mono- and bisperoxo complexes of MTO after the addition of H_2O_2 to complex **8**. The ratio of mono- and bisperoxo complexes is dependent on the amount of H_2O_2 applied[13] which confirms again the complete dissociation of the ligand when the catalytically active species is formed.

Raman analysis suggests that in all of the cases examined the final products in the presence of a high excess (>50:1) of H_2O_2 are bisperoxo complexes. It should be noted, however, that Raman spectroscopy may not be sensitive enough to detect the monoperoxo intermediates if they are formed only in tiny amounts within an equilibrium.

Conclusions

Several bidentate Lewis base adducts of MTO, often sensitive to light, were synthesized and fully characterized. In an exemplary study, the X-ray crystal structure of one of the complexes was determined. The ^1H, ^{13}C, and ^{17}O NMR data of the bidentate Lewis base adducts of MTO are in good accord with the pK_a values of the Lewis bases. The higher the pK_a values, the stronger the Re−ligand interaction. Weak ligand coordination leads to fluxional structures in solution and to ligand-exchange reactions. X-ray crystallography and vibrational spectroscopy are less sensitive to subtle changes in the Re−N interactions than is NMR spectroscopy. The bidentate Lewis base complexes of MTO react with excess H_2O_2 to form peroxo complexes. While the weakly coordinating ligand 2,2′-bipyrimidine is dissociated after the addition of excess H_2O_2, the more strongly coordinating bidentate nitrogen donor ligands seem to undergo a change to monodentate on the addition of H_2O_2. The Lewis base ligands are, in this case, still coordinated to the Re center and can, therefore, influence the catalytic activity significantly.

Considering these findings, it appears that aromatic bidentate Lewis base adducts of MTO do not display significant advantages over aromatic monodentate Lewis base ligands with respect to their activity in olefin epoxidation and to the stability of their peroxo species. Due to the higher steric demand and the chelating effect of the bidentate Lewis bases, higher excesses of the oxidizing agent are necessary to shift the equilibrium toward the catalytic active peroxo species. Raising the reaction temperature accelerates not only the catalytic reaction but also the catalyst decomposition. Below room temperature the catalyst decomposition is negligible; above room temperature it becomes increasingly important. In solvents with higher dielectric constants, the catalytic system is more active due to the presence of higher amounts of the more active oxidant, HO_2^-. In solvents with lower dielectric constants, a higher excess of Lewis base is required to reach comparable product yields.

Acknowledgment. W.-M.X. acknowledges the Bayerische Forschungsstiftung for a postdoctoral grant. P.F. and E.B. are grateful to the Alexander von Humboldt foundation for postdoctoral fellowships. We also acknowledge the Fonds der Chemischen Industrie (FCI) and Prof. Dr. W. A. Herrmann for continuous support. Dr. M. Groarke and Dr. A. M. Santos are acknowledged for helpful discussions.

Supporting Information Available: An X-ray crystallographic file for compound **5** in CIF format and Raman data for selected compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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