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Rhenium(V) Oxo Complexes with Acetylacetone Derived Schiff Bases: Structure and Catalytic Epoxidation

Anna Sachse,[#] Nadia C. Mösch-Zanetti,*[,†] Ganna Lyashenko,[†] J. Wolfram Wielandt,[†] Kerstin Most,[#] Jörg Magull,[#] Fabio Dall'Antonia,[†] Aritra Pal,[#] and Regine Herbst-Irmer[#]

Institut für Chemie, Karl-Franzens-Universität, Schubertstrasse 1, A-8010 Graz, Austria, and Institut für Anorganische Chemie, Georg-August-Universität, Tammannstrasse 4, D-37077 Göttingen, Germany

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Substitution reactions of rhenium(V) oxo precursors $[ReOCl_3(PPh_3)_2]$ or $[NBu_4][ReOCl_4]$ with the bidentate acetylacetone-derived ketoamine ligands APOH = 4-anilino-3-penten-2-one, DPOH = 4-[2,6-dimethylanilino]-3-penten-2-one, and MTPOH = 4-[2-(methylthio)anilino]-3-penten-2-one gave the complexes $[ReO(APO)Cl_2(PPh_3)]$ (**1**), $[ReO(DPO)Cl_2(PPh_3)]$ (**2**), and $[NBu_4][ReOLCl_3]$ (**3**, L = APO; **4**, L = DPO; **5**, L = MTPO), respectively. All complexes exhibit only one ketoamino chelate, independent of the amount of ligand added to the rhenium precursors. The complexes were characterized by ^1H and ^{13}C NMR spectroscopy. X-ray crystal structures of the complexes **1**, **2**, **4**, and **5**, including that of MTPOH, were determined, revealing the *trans* position of the two oxygen atoms and the *trans*-Cl,Cl conformation in **1** and **2**, in contrast to most other rhenium complexes of this type where the *cis*-Cl,Cl conformation is observed. Coordination of the potentially tridentate ligand MTPOH in **5** is bidentate with a dangling thioether substituent. Compound **2** shows catalytic activity in the oxidation of *cis*-cyclooctene with *tert*-butylhydroperoxide.

Introduction

Rhenium(V) oxo complexes that contain Schiff base ligands derived from salicylaldehyde have been known since the first description in 1979 by Wilkinson and co-workers.[1] Ever since then, they have attracted considerable interest mainly because of the use of the nuclide ^{186}Re in radiotherapy.[2,3] Various ligand derivatives were investigated including bi-, tri-, and tetradentate versions.[1,4−14] Schiff base ligands derived from acetylacetone are widely employed in coordination chemistry because of their convenient tuning of steric and electronic properties. Thus, it is surprising that rhenium oxo complexes with such ligands were by far less studied than other systems.[1,15−17] Recent investigations on such ligands by Jurisson and co-workers revealed unexpected coordination chemistry and reactivity.[16,17]

The important chemical features of rhenium oxo complexes include their use as oxidation catalysts and their

* To whom correspondence should be addressed. E-mail: nadia.moesch@uni-graz.at.
† Karl-Franzens-Universität.
# Georg-August-Universität.

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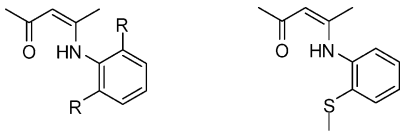
capability to transfer an oxygen atom (OAT) to suitable organic substrates.[18−21] The epoxidation of olefins has been most thoroughly investigated in the past decade, where mainly high oxidation state rhenium(VII) catalysts were employed,[22−25] and only rarely rhenium(V) compounds.[9,26,27] Espenson and co-workers found OAT reactivity from pyridine-*N*-oxide to phosphines.[20] Detailed research on OAT reactions involving Re(V) oxo complexes where the ligands represent oxazoline-derivatized phenolates is reported by Abu-Omar and co-workers.[19,28−30] Many of these rhenium(V) oxidation catalysts contain salicylate-based ligands. In contrast, acetylacetone-based ligands have not been employed yet. Our ongoing interest in oxidation reactions[31−34] prompted us to investigate rhenium(V) oxo complexes with the β-ketoamine ligands 4-anilino-3-penten-2-one (APOH), (4-[2,6-dimethylanilino]-3-penten-2-one (DPOH), and 4-[2-(methylthio)anilino]-3-penten-2-one (MTPOH). Here, the syntheses, crystallographic characterization, and reactivity in oxidation reactions of such complexes are reported.



Experimental Section

All manipulations were carried out under dry nitrogen using standard Schlenk line or glove box techniques. All solvents were purified by standard methods and distilled under a nitrogen atmosphere immediately prior to use. $[ReOCl_3(PPh_3)_2]$,[35] $[NBu_4][ReOCl_4]$,[36,37] APOH, and DPOH[38] were prepared according to literature procedures. All other chemicals mentioned were used as purchased from commercial sources.

Samples for mass spectrometry were measured on a BIO-RAD Digilab FTS-7 mass spectrometer with a Finnigan MAT 95, and all NMR spectra were recorded on a Bruker Avance 500 or 200 MHz spectrometer. Elemental analyses were performed by the Analytisches-Chemisches Laboratorium des Instituts für Anorganische Chemie in Göttingen, Germany.

X-ray Crystallographic Determinations. Crystals of compounds **1**, **2**, **4**, and **5** were taken from the solution, covered with oil, and mounted on glass fibers at room temperature. Data for compounds **2**, **4**, and **5** were collected on a Stoe IPDS II-array detector system instrument with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å); data for **1** were recorded on a Bruker three-circle diffractometer equipped with a SMART 600 area detector with Cu Kα radiation (λ = 1.54178 Å), and data for MTPOH were recorded on a Stoe-Siemens-Huber four-circle diffractometer equipped with a CCD detector with Mo Kα radiation (λ = 0.71073 Å). The structures were solved by direct methods using SHELXS-97[39] and refined against F^2 on all data by full-matrix least-squares with SHELXL-97.[40] All non-hydrogen atoms were refined anisotropically. All hydrogen atom bonds to carbon were included in the model at geometrically calculated positions and refined using a riding model. The hydrogen atom bound to nitrogen in MTPOH was refined freely with a distance restraint. The THF group in **1** was disordered about two positions and was refined with distance restraints and restraints for the anisotropic displacement parameters. The crystal of MTPOH was non-merohedrally twinned with the twin law −1 0 0 0−1 0 0.79 1 1. The fractional contribution of the minor domain refined to 0.168(1).

Synthesis of MTPOH. This compound was previously prepared by direct condensation of acetylacetone and 2-(methylthio)aniline.[41,42] This procedure gave no satisfactory yields in our hands; therefore the following procedure was applied.

Acetylacetone (5.0 g, 49.7 mmol) and sodium hydride (2 equiv, 2.4 g, 100 mmol) were dissolved in 150 mL of diethyl ether at 0 °C. The mixture was warmed to room temperature and was stirred for 5 h. After filtration over Celite, the volume of the solvent was reduced by half; 5.43 g (49.9 mmol) of trimethylsilylchloride was added, and the mixture was stirred for 18 h at room temperature. Evaporation of the solvent gave crude trimethylsilyl acetylacetone (acac($SiMe_3$)) (6.96 g, 80%). ^{1}H NMR (300 MHz, C_6D_6): δ 0.09 (s, 9 H, SiMe3), 1.73 (s, 3 H, Me), 2.15 (s, 3 H, Me), 6.23 (s, 1 H, γ-H). This material was used in the subsequent reaction. 2-(Methylthio)aniline (5.65 g, 40.6 mmol) was added to a solution of acac($SiMe_3$) (5.81 g, 33.7 mmol) in 100 mL of toluene, and the mixture was stirred at reflux for 3 h. After the mixture was cooled to room temperature, the solvent was removed, and the residual oil was fractionally distilled. The product MTPOH distilled at 115 °C at 10^{-3} mbar as a yellow oil, which crystallized after it was stored at room temperature (4.03 g, 54%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.89 (s, 3 H, Me), 2.13 (s, 3 H, Me), 2.43 (s, 3 H, SMe), 5.25 (s, 1 H, γ-H), 7.0−7.3 (m, 4 H, Ar), 12.28 (br s, 1 H,

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NH). ^{13}C NMR (125 MHz, C_6D_6): δ 14.6 (*C*H_3), 19.1 (*C*H_3), 29.2 (*C*H_3), 98.0 (s, 1 H, *C*H), 125.0, 126,2, 126,8, 127.0, 136.7, 137.0 (*C*-Ar), 159.8, 195.8. MS (*m*/*z* (%)): 221 (100) [M^+], 206 (65) [M^+ − Me]. Anal. Calcd for $C_{12}H_{15}NOS$: C, 65.12; H, 6.83; N, 6.33. Found: C, 65.2; H., 7.0; N, 6.5.

Synthesis of [ReO(APO)Cl$_2$(PPh$_3$)] (1). A solution of 0.18 g (1.0 mmol) of APOH and 0.5 mL (3.6 mmol) of NEt_3 in 20 mL of toluene was added to a suspension of 0.83 g (1.0 mmol) of [$ReOCl_3$-(PPh_3)$_2$] in 40 mL of toluene. The mixture was stirred under reflux for 2 h. The green solution was filtered over Celite, and the solvent was removed in vacuo. The remaining green solid was washed with diethyl ether giving 0.49 g (69%) of the product. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.65 (s, 3 H, C*H*$_3$CO), 2.33 (s, 3 H, C*H*$_3$CN), 5.48 (s, 1 H, γ-H), 6.8−7,1 (m, 12 H, *H*-Ar and *H*-ArP), 7,84 (d, 2 H, ortho *H*-Ar), 7,98 (m, 6 H, ortho *H*-ArP). ^{13}C NMR (75 MHz, C_6D_6): δ 22,25 (*C*H_3CO), 23.35 (d, ^4J(P,C) = 4.2 Hz, *C*H_3CN), 100.82 (γ-C), 125.13 (para *C*Ar), 127.54 (meta *C*Ar), 128.47 (para *C*ArP), 129.13 (ortho CAr), 130.98 (d, ^3J(P,C) = 2.6 Hz, meta *C*ArP), 131.61 (d, ^1J(P,C) = 54 Hz, *C*P), 135.30 (d, ^2J(P,C) = 9 Hz, ortho *C*ArP), 153.39 (d, ^3J(P,C) = 1.7 Hz, *C*NAr), 171.0 (d, ^3J(P,C) = 1.4 Hz, *C*N), 177.48 (d, ^3J(P,C) = 2.3 Hz, *C*O). ^{31}P NMR (200 MHz, $CDCl_3$): δ −5.5. MS (EI, *m*/*z*, (%)): 737 (1) [$M]^+$, 262 (100) [PPh_3]. Anal. Calcd for $C_{29}H_{27}NCl_2O_2PRe$·THF: C, 50.70; H, 4.51; N, 1.79. Found: C, 50.69; H, 4.40; N, 1.83%.

Synthesis of [ReO(DPO)Cl$_2$(PPh$_3$)] (2). A solution of 0.12 g (0.59 mmol) of DPOH and 1.2 mL (7.9 mmol) of NEt_3 in 20 mL of toluene was added to a suspension of 0.5 g (0.6 mmol) of [$ReOCl_3$(PPh_3)$_2$] in 40 mL of toluene. The mixture was stirred for 24 h at room temperature. The green solution was filtered over Celite, and the solvent was removed in vacuo. The remaining green solid was washed with diethyl ether and recrystallized from THF at −25 °C, giving 0.31 g (70%) of the product. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.70 (s, 3 H, C*H*$_3$CO), 2.49 (s, 6 H, C*H*$_3$Ar), 2.63 (s, 3 H, C*H*$_3$CN), 5.83 (s, 1 H, γ-H), 7,1 (m, 3 H, *H*-Ar), 7,4 (m, 9 H, meta/para *H*-ArP), 7,8 (m, 6 H, ortho *H*-ArP). ^{13}C NMR (126 MHz, $CDCl_3$): δ 19.97 (*C*H_3Ar), 22,08 (*C*H_3CO), 23.71 (d, ^4J(P,C) = 3.8 Hz, *C*H_3CN), 105.11 (γ-C), 127.04 (para *C*NAr), 128.14, (d, ^3J(P,C) = 11 Hz, meta *C*ArP), 128.72 (para *C*ArP), 130.19 (d, ^1J(P,C) = 53 Hz, C_{ipso} PAr), 130.82 (meta *C*NAr), 133.81 (C_{ipso} NAr), 134.62 (d, ^2J(C,P) = 9.4 Hz, ortho *C*ArP), 133.07 (149.45 (*C*NAr), 174.28 (*C*N), 177.22 (*C*O). ^{31}P NMR (200 MHz, $CDCl_3$): δ 5.89. MS (EI, *m*/*z*, (%)): 737 (1) [$M]^+$, 475 (20) [M − PPh_3], 262 (100) [PPh_3]. Anal. Calcd for $C_{31}H_{31}NCl_2O_2PRe$: C, 50.47; H, 4.42; N, 1.90. Found: C, 50.44; H, 4.52; N, 2.06%.

Synthesis of [ReO(APO)Cl$_3$][NBu$_4$] (3). A solution of 0.18 g (1.0 mmol) of APOH and 0.5 mL (3.6 mmol) of NEt_3 in 15 mL of EtOH was added to a solution of 0.58 g (1.0 mmol) of [NBu_4]-[$ReOCl_4$] in 20 mL of EtOH. The mixture was stirred for 2 h at room temperature. The green solution was filtered over Celite, and the solvent was removed in vacuo. The remaining green solid was washed with diethyl ether and pentane giving 0.37 g (51%) of the product. ^{1}H NMR (300 MHz, C_6D_6): δ 0.92 (m, 12 H, C*H*$_3$ Bu), 1.05 (br, 8 H, CH$_3$C*H*$_2$ Bu), 1.32 (br, 8 H, CH$_3$CH$_2$C*H*$_2$ Bu), 2.63 (s, 3 H, C*H*$_3$CO), 2.88 (s, 3 H, C*H*$_3$CN), 3.21 (br, 8 H, C*H*$_2$N Bu), 5.52 (s, 1 H, γ-H), 6.94 (t, 1 H, Ar), 7.09 (t, 2H, Ar), 7.62 (d, 2 H, Ar). ^{13}C NMR (125 MHz, C_6D_6): δ 14.14 (*C*H$_3$ Bu), 20.26 (CH$_3$*C*H$_2$ Bu), 21.88 (*C*H$_3$CO), 22.76 (*C*H$_3$CN), 24.53 (CH$_3$-CH$_2$*C*H$_2$ Bu), 59.32 (*C*H$_2$N Bu), 98.11 (γ-C), 124.12, 126.07, 128.29, 157.94 (*C*NAr), 175.40 (*C*N), 179.08 (*C*O). Anal. Calcd for $C_{27}H_{48}N_2Cl_3O_2Re$: C, 44.71; H, 6.67; N, 3.86. Found: C, 44.37; H, 6.59; N, 3.63%.

Synthesis of [ReO(DPO)Cl$_3$][NBu$_4$] (4). A solution of 0.087 g (0.43 mmol) of DPOH and 7 mL (50 mmol) of NEt_3 in 15 mL of THF was added to a solution of 0.25 g (0.43 mmol) of [NBu_4]-[$ReOCl_4$] in 20 mL of THF. The mixture was stirred for 12 h at room temperature. The green solution was filtered over Celite, and the solvent was removed in vacuo. The remaining green solid was washed with diethyl ether and pentane and recrystallized from THF/pentane at −25 °C giving 0.28 g (86%) of the product. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.9 (m, 12 H, C*H*$_3$ Bu), 1.33 (br, 8 H, CH$_3$C*H*$_2$ Bu), 1.51 (br, 8 H, CH$_3$CH$_2$C*H*$_2$ Bu), 2.42 (s, 6 H, C*H*$_3$-Ar), 2.60 (s, 3 H, C*H*$_3$CO), 2.91 (s, 3 H, C*H*$_3$CN), 3.09 (br, 8 H, C*H*$_2$N Bu), 5.75 (s, 1 H, γ-H), 6.93 (m, 3 H, Ar). ^{13}C NMR (125 MHz, $CDCl_3$): δ 13.69 (*C*H$_3$ Bu), 19.64 (CH$_3$*C*H$_2$ Bu), 19.77 (*C*H$_3$-Ar), 22.06 (*C*H$_3$CO), 22.43 (*C*H$_3$CN), 24.08 (CH$_3$CH$_2$*C*H$_2$ Bu), 58.99 (*C*H$_2$N Bu), 101.18 (γ-C), 125.85, 127.95, 132.23, 153.39 (*C*NAr), 177.41 (*C*N), 178.64 (*C*O). Anal. Calcd for $C_{29}H_{52}N_2Cl_3O_2$-Re·3H_2O: C, 43.16; H, 7.24; N, 3.46. Found: C, 43.37; H, 7.07; N, 3.31%.

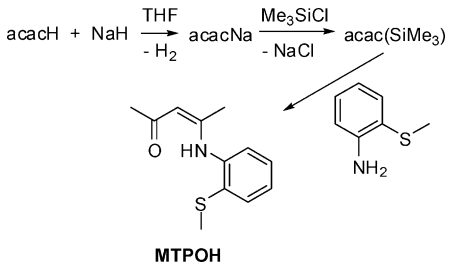
Synthesis of [ReO(MTPO)Cl$_3$][NBu$_4$] (5). A solution of MTPOH (0.094 g, 0.44 mmol) in THF was cooled to −78 °C, and after the addition of 1 equiv of *n*-BuLi by syringe, the mixture was stirred for 30 min. This solution was added to a solution of 0.25 g (0.43 mmol) of [NBu_4][$ReOCl_4$] in 20 mL of THF by cannula, and the mixture was stirred for 2 h at room temperature. The dark suspension was filtered over Celite, and the solvent was removed in vacuo. The remaining green solid was recrystallized from THF at − 25 °C giving 0.20 g (62%) of the product. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.9 (m, 12 H, C*H*$_3$ Bu), 1.33 (br, 8 H, CH$_3$C*H*$_2$ Bu), 1.60 (br, 8 H, CH$_3$CH$_2$C*H*$_2$ Bu), 2.40 (s, 3 H, C*H*$_3$-CO), 2.67 (s, 3 H, C*H*$_3$CN), 3.05 (s, 3 H, SC*H*$_3$), 3.09 (br, 8 H, C*H*$_2$N Bu), 5.76 (s, 1 H, γ-H), 7.1 (m, 3 H, Ar), 7.6 (m, 1 H, Ar). ^{13}C NMR (125 MHz, $CDCl_3$): δ 12.8 (*C*H$_3$ Bu), 14.9 (CH$_3$), 19.03 (CH$_3$*C*H$_2$ Bu), 20.6 (CH$_3$), 22.6 (CH$_3$), 23.6 (CH$_3$CH$_2$*C*H$_2$ Bu), 60.3 (*C*H$_2$N Bu), 94.8 (γ-C), 122.9, 124.2, 125.1, 127.1, 131.3, 152.5 (*C*NAr), 176.0 (*C*N), 188.8 (*C*O). Anal. Calcd for $C_{28}H_{50}N_2Cl_3O_2$-ReS: C, 43.60; H, 6.53; N, 3.63. Found: C, 43.92; H, 6.75; N, 3.63%.

Catalytic Reactions. The catalytic reactions were performed under an atmosphere of nitrogen. The reaction vessel was immersed into an oil bath, and a solution of 0.3 g (2.7 mmol) of *cis*-cyclooctene dissolved in 5 mL of $CHCl_3$, 0.3 g (2.3 mmol) dibutyl ether as an internal standard, and 0.05 g (6.9 10^{-5} mol, 3 mol % vs the olefin) of **2** were added, and the mixture was heated to 50 °C. The peroxide (0.75 mL of 5.5 M solution of TBHP in *n*-decane, 1.5 equiv) was added by syringe to the heated solution at once. Samples were withdrawn every 10 min; a small amount of manganese dioxide added to destroy excess TBHP, and the mixture was filtered over a small pad of Celite and analyzed using a GC-MS. The product was quantified versus the internal standard.

Results and Discussion

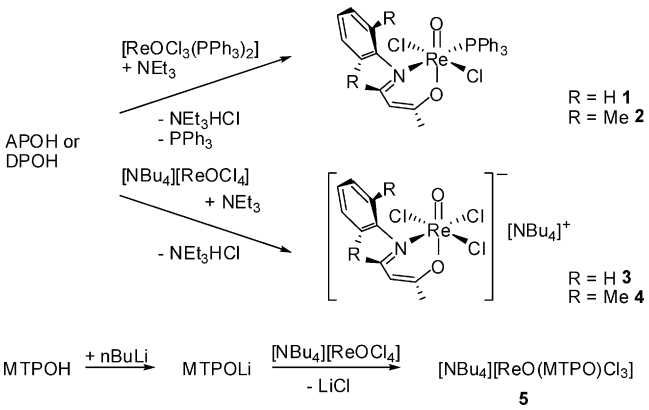
The ligands APOH and DPOH were prepared by direct condensation of acetylacetone and the appropriate amine.[38] For the MTPOH ligand, a similar method of preparation was reported.[41,42] However, this procedure did not give satisfactory yields in our hands. Thus, for the preparation of MTPOH, acetylacetone was activated by silylation prior to the condensation as shown in Scheme 1. Spectroscopic characterization, as well as X-ray crystal structure analysis, of a single crystal confirmed the formation of MTPOH. Whereas APOH and DPOH have been extensively employed in various metal complexes, only few examples are known with MTPOH, and none of these are with rhenium.[42,43]

Scheme 1



MTPOH

Scheme 2



Two types of rhenium(V) oxo complexes containing APO^- or DPO^- were synthesized starting from the two common starting materials, either from $[ReOCl_3(PPh_3)_2]$ or $[NBu_4][ReOCl_4]$ in the presence of excess triethylamine as shown in Scheme 2. The reaction conditions employed for the syntheses of the individual compounds varied depending on the ligand. Green compound $[ReO(APO)Cl_2(PPh_3)]$ (**1**) can conveniently be prepared by the addition of APOH/NEt_3 to $[ReOCl_3(PPh_3)_2]$ in toluene solution under refluxing conditions for 2 h. For compound $[ReO(DPO)Cl_2(PPh_3)]$ (**2**), better yields are obtained when the analogous reaction employing DPOH/NEt_3 and $[ReOCl_3(PPh_3)_2]$ is performed in toluene at room temperature with reaction times that are typically in the range of 24 h. The reactions can be conveniently monitored by TLC on silica with $CHCl_3$ as eluent detecting the presence or absence of free ligands, respectively. The absence of free ligand points to complete conversion. The complexes themselves did not elute under these conditions. To increase the reaction rate for the preparation of **2** refluxing toluene conditions were investigated. This resulted in the formation of unidentified reaction mixtures as revealed by ^1H NMR spectroscopy. We were not able to isolate any pure compound from such mixtures. However, the observed color change to brown is indicative of a reduction process. Presumably, the presence of triphenylphosphine in the reaction solution (coming from the starting material $[ReOCl_3(PPh_3)_2]$) reduced the Re(V)═O center to paramagnetic Re(III) at elevated temperatures. Such reactivity was recently reported by Jurisson and co-workers for the compound [ReLOCl], where L represents a tetradentate acetylacetone-derived ligand.[17] They report on the reduction to $[ReL(PPh_3)_2][PF_6]$ in the presence of PPh_3 under refluxing conditions.

The green compounds $[NBu_4][ReO(APO)Cl_3]$ (**3**) and $[NBu_4][ReO(DPO)Cl_3]$ (**4**) were prepared by the addition of mixtures of APOH/NEt_3 and DPOH/NEt_3, respectively, to a solution of $[NBu_4][ReOCl_4]$ in THF in high yield. The compounds are soluble in polar solvents such as THF and $CHCl_3$ but are insoluble in diethyl ether. These complexes are surprisingly resistant toward substitution of a second chlorine atom by an additional ligand APO^- or DPO^-, respectively. Thus, all experiments (variation of the solvent to ethanol, employing lithium salts of the ligands, or refluxing conditions) trying to obtain compounds of the type $[ReOL_2Cl]$ were unsuccessful, both starting from $[ReOCl_3(PPh_3)_2]$ and $[NBu_4][ReOCl_4]$. With one exception, mass spectrometry of crude reaction mixtures gave no evidence for the formation of a disubstituted species. Only the mass spectrum of a reaction mixture of 2 equiv of the least sterically demanding ligand APOH/NEt_3 with $[ReOCl_3(PPh_3)_2]$ revealed a signal indicative of the compound $[ReO(APO)_2Cl]$ showing that in principle such a species would be accessible. However, because the NMR spectrum of the reaction mixture gave no indication for another compound in solution but **1**, the putative $[ReO(APO)_2Cl]$ is apparently formed only in trace amounts. This is in contrast to the reactivity with bidentate salen-type ligands[9,29] and tri- and tetradentate acetylacetone-derived ligands, where complexes of the type [ReOLL′Cl] were obtained.[16,44] Crystal structure analyses of compounds **1** and **2** show the two chlorine atoms occupying *trans* positions to each other (vide infra), which is possibly the reason for the lack of reactivity toward a second substitution. In the hope to force the two Cl atoms into a *cis* position to each other, thereby changing the reactivity, the potentially tridentate ligand MTPOH was prepared. A facial coordination of this ligand would lead to a chlorine atom *trans* to the additional donor hopefully weakening the metal chlorine bond and thus allowing the preparation of a complex $[ReO(L)_2Cl]$. The method of choice for its coordination proved to be the conversion to the lithium salt MTPOLi prior to the reaction with a rhenium(V) precursor. The addition of MTPOLi to $[NBu_4][ReOCl_4]$ in THF at room temperature leads to the monosubstituted compound $[NBu_4][ReO(MTPO)Cl_3]$ (**5**) in moderate yields. Other methods that were successful for the preparation of complexes **1**−**4** did not yield in any pure compound, and again, no evidence for a disubstituted compound could be obtained. It is interesting to note that the method of preparation is crucial even though the structure of the ligands and therefore the obtained compounds are similar. This indicates that small changes of steric and electronic properties in the ligand have a significant impact on the reactivity of the resulting compounds emphasizing the importance of investigations such as those described in this work. More drastic conditions, for example, higher temperatures, would favor the disubstitution but increase the rate of formation of reduced byproducts.

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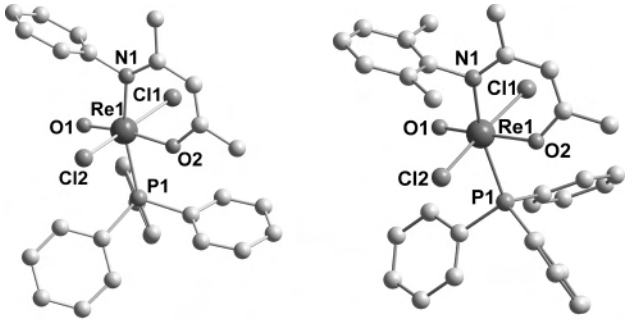


Figure 1. Molecular views of **1** (left) and **2** (right) with selected atom numbering showing the coordination at the rhenium center to be isostructural. Hydrogen atoms are omitted for clarity.

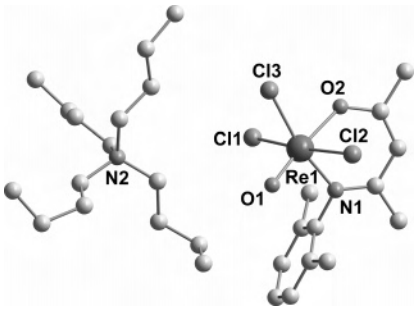


Figure 2. Molecular view of **4** with selected atom numbering. Hydrogen atoms are omitted for clarity.

NMR spectroscopic data, as well as mass spectrometry, confirm the formation of compounds **1**−**5**. In all cases, ^{1}H NMR and ^{13}C NMR spectra show one set of resonances for a coordinated ligand as expected for monosubstituted compounds. The assignment of the resonances is mainly based on comparison to the spectra of the free ligands. To assign the two methyl groups in the backbone, the resonances were compared to those of a similar ligand, where one of the methyl groups is substituted by a phenyl group (ArNC(Me)-CHC(Ph)O).[44] The resonances of the NCMe group in the ^{1}H NMR spectra of neutral rhenium(V) complexes are reported between 2.7 and 3 ppm.[44] This allows us to distinguish the two resonances for the methyl groups in **1** and **2**: singlets at 1.6 and 1.7 ppm can be assigned to the methyl group closer to oxygen (OCMe), whereas those at 2.3 and 2.6 to the ones closer to nitrogen (NCMe). The higher-electron density at the metal center of the anionic complexes **3**−**5** shifts the corresponding resonances to lower field (2.4−2.6 ppm for OCMe and 2.7−2.9 ppm for NCMe). For the assignment of the resonances in the ^{13}C{^{1}H} NMR spectra, a DEPT experiment for compound **2** was recorded allowing the assignment of all resonances. In addition, coupling to the ^{31}P nucleus helped in the assignment of the resonances in the aromatic region. Thus, doublets at 128.14 (J = 11 Hz), 130.19 (J = 53 Hz), and 134.62 (J = 9 Hz) are assigned to the C_{meta}, C_{ipso}, and C_{ortho} atoms, respectively, of the coordinated PPh_3 ligand.

X-ray Crystal Structures. Molecular structures of compounds **1**, **2**, **4**, and **5**, as well as of the ligand MTPOH, were determined by X-ray crystallography and are displayed in Figures 1−4. Selected bond lengths and angles are given in Table 1, and crystallographic data are presented in Table 2. The overall geometry in all four rhenium compounds is distorted octahedral, and the oxygen atom of the ligand is in *trans* position to the Re═O group. This is similar to the coordination mode with salicylaldimine-derived ligands where the relatively hard phenoxide ligand occupies the *trans* position to Re═O, regardless of of the denticity of the ligand.[8,9,13] However, there is no apparent consistency because there are several structures with other geometries. For example, in complexes of the type [ReOLCl(PPh_3)] with a tridentate ligand, the position *trans* to Re═O is occupied by a chlorine atom.[45] In addition, in the previously reported

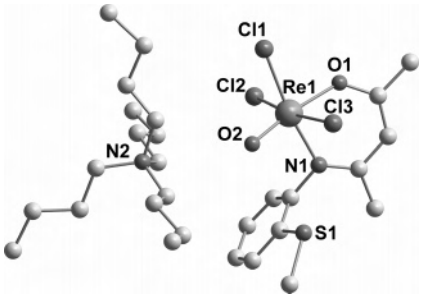


Figure 3. Molecular view of **5** with selected atom numbering. Hydrogen atoms are omitted for clarity.

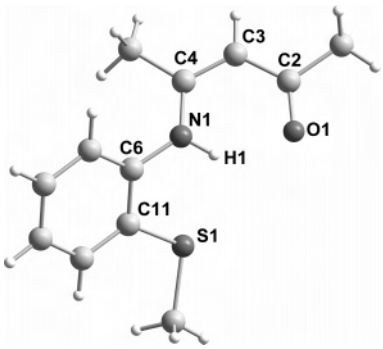


Figure 4. Molecular view of MTPOH.

Table 1. Selected Bond Lengths (Å) and Angles (deg) of Compounds [ReO(APO)Cl_2(PPh_3)] (**1**), [ReO(DPO)Cl_2(PPh_3)] (**2**), [NBu_4][ReO(DPO)Cl_3] (**4**), and [NBu_4][ReO(MTPO)Cl_3] (**5**)

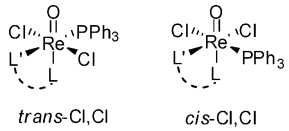
	1	**2**	**4**	**5**
Re1−O1	1.682(2)	1.668(5)	1.669(2)	1.667(3)
Re1−O2	2.002(2)	2.010(3)	2.033(2)	2.016(3)
Re1−N1	2.105(2)	2.124(3)	2.114(3)	2.142(4)
Re1−P1	2.475(1)	2.474(1)		
Re1−Cl1	2.395(1)	2.414(1)	2.385(1)	2.405(1)
Re1−Cl2	2.385(1)	2.376(1)	2.419(1)	2.383(1)
Re1−Cl3 *trans* to N			2.384(1)	2.376(1)
N1−C1	1.312(3)	1.321(5)	1.327(4)	1.318(6)
O1−Re1−O2	170.26(8)	170.6(1)	172.9(1)	171.8(2)
O1−Re1−N1	106.23(8)	102.2(1)	95.0(1)	91.3(2)
O1−Re1−Cl1	94.30(7)	89.2(1)	95.3(1)	91.5(1)
O1−Re1−Cl2	95.30(7)	96.8 (1)	90.1(1)	97.7(1)
O1−Re1−P1 or Cl3	88.66(6)	92.1(1)	97.4(1)	98.2(1)
O2−Re1−N1	83.50(8)	82.8(1)	82.3(1)	82.5(1)
O2−Re1−Cl1	85.89(6)	83.1(1)	91.3(1)	83.1(1)
O2−Re1−Cl2	85.60(6)	91.1(1)	83.3(1)	87.7(1)
O2−Re1−P1 or Cl3	81.60(6)	83.0(1)	85.4(1)	88.1(1)
N1−Re1−P1 or Cl3	164.88(6)	165.7(1)	167.6(1)	170.3(1)
N1−Re1−Cl1	85.32(6)	86.7(1)	91.8(1)	89.4(1)
N1−Re1−Cl2	86.56(6)	90.9(1)	87.9(1)	90.2(1)
Cl1−Re1−Cl2	168.84(2)	173.9(1)	174.6(1)	170.8(1)
Cl1−Re1−P1 or Cl3	91.04(2)	93.3(1)	87.4(1)	91.8(1)
Cl2−Re1−P1 or Cl3	94.84(2)	87.8(1)	91.8(1)	87.1(1)

Table 2. Crystallographic Data and Structure Refinement of $[ReO(APO)Cl_2(PPh_3)]$ (**1**), $[ReO(DPO)Cl_2(PPh_3)]$ (**2**), $[NBu_4][ReO(DPO)Cl_3]$ (**4**), $[NBu_4][ReO(MTPO)Cl_3]$ (**5**), and MTPOH

	1	**2**	**4**	**5**	MTPOH
M	781.69	881.85	753.28	889.48	221.31
formula	$C_{29}H_{27}Cl_2NO_2PRe\cdot THF$	$C_{31}H_{31}Cl_2NO_2PRe\cdot 2THF$	$C_{29}H_{52}Cl_3N_2O_2Re$	$C_{28}H_{50}Cl_3N_2OReS\cdot THF\cdot 0.5tol$	$C_{12}H_{15}NOS$
T (K)	100(2)	133(2)	133(2)	133(2)	133(2)
cryst syst	monoclinic	triclinic	monoclinic	monoclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$	$P2_1/c$	$P2_1/n$	$P\bar{1}$
a (Å)	9.048(3)	15.6414(7)	13.4531(9)	14.5256(6)	7.828(2)
b (Å)	21.650(3)	15.8201(7)	16.9556(13)	17.4906(6)	8.018(2)
c (Å)	15.583(3)	16.4334(8)	15.5468(10)	17.1378(8)	10.210(2)
α (deg)	90	109.916(4)	90	90	112.79(3)
β (deg)	91.75(3)	91.352(4)	113.560(5)	113.981(3)	106.59(3)
γ (deg)	90	93.144(3)	90	90	92.62(3)
U (Å^3)	3051(1)	3813.6(3)	3250.7(4)	3978.2(3)	557.3(2)
Z	4	4	4	4	2
D_c (mg m^{-3})	1.702	1.536	1.538	1.485	1.319
μ (mm^{-1})	10.178	3.408	4.012	3.343	0.263
F(000)	1552	1776	1528	1820	236
2θ range (deg)	3.50−59.14	1.54−24.79	1.65−24.81	1.56−24.83	2.29−27.68
measured reflns	30 888	36 030	11 695	38 550	11 768
unique reflns	4362 [R_{int} = 0.0372]	13 038 [R_{int} = 0.0380]	5258 [R_{int} = 0.0317]	6807 [R_{int} = 0.0723]	3305 [R_{int} = 0.0952]
obsd reflns [$I > 2\sigma(I)$]	4060	10994	4551	5622	3047
data/restraints/params	4362/47/382	13028/0/797	5258/0/342	6807/2/396	3305/1/144
GOF on F^2	1.046	1.023	0.957	1.012	1.087
final R indices [$I > 2\sigma(I)$]	R1 = 0.0175	R1 = 0.0274	R1 = 0.0234	R1 = 0.0343	R1 = 0.0560
	wR2 = 0.0424	wR2 = 0.0703	wR2 = 0.0535	wR2 = 0.0802	wR2 = 0.1583
R indices (all data)	R1 = 0.0197	R1 = 0.0355	R1 = 0.0299	R1 = 0.0465	R1 = 0.0608
	wR2 = 0.0433	wR2 = 0.0732	wR2 = 0.0551	wR2 = 0.0839	wR2 = 0.1642
largest diff. peak, hole (e Å^{-3})	0.536, −0.405	1.086, −1.208	0.519, −1.363	0.823, −0.861	0.533, −0.534

structures of [ReOLCl] complexes with tetradentate acetylacetone-derived ligands, a linear O═Re−Cl bond is found.[16] This is in contrast to the structures reported herein with bidentate acetylacetone-derived ligands pointing to a fine balance between steric and electronic factors for a preferred geometry. Thus, in the absence of steric restraint, hard donors occupy the *trans* position to Re═O. The Re═O, Re−O, and Re−N bond lengths in the four complexes are consistent with mononuclear rhenium(V) oxo Schiff base complexes.[7,9,11,46]

Compounds **1** and **2** should be compared to previously reported structures of the type $[ReO(LL')Cl_2(PPh_3)]$ where LL′ represents either a monoanionic bidentate ligand or two monodentate ligands one of them being monoanionic and the other one neutral.[6,12,47−51]



In all reported compounds, the oxygen donor is located *trans* to the oxo group, but the position of the chlorine atoms relative to each other differ being either *trans* as found in **1** and **2** or *cis* as found in the majority of the structures. The *trans*-Cl,Cl conformation has only rarely been found in this type of complex.[51] Thus, the *trans* situation in **1** and **2** is from a electronical point of view surprising, but apparently the higher steric bulk of the substituent on nitrogen forces the large triphenylphosphine ligand into the *trans* position.

The MTPO ligand in compound **5** is 2-coordinate with a dangling thioether functionality because all distances from the sulfur atom to the metal or other neighboring atoms are too large for bonding interactions (e.g., Re1···S1 = 4.008 Å, S1···O1 = 3.324 Å). The Re−SRR′ bond lengths are typically in the range of 2.4−2.5 Å.[52−54] The coordination of MTPO causes the N−C(phenyl) bond to rotate (torsion angle C2−N1−C6−C7 = 94.1(1)°), so that the ligand plane and the phenyl plane are almost normal to each other, preventing coordination. Figure 4 displays the molecular structure of MTPOH which shows the ligand to be in its keto tautomeric form with the hydrogen atom H1 attached to the nitrogen atom. The torsion angle C4−N1−C6−C11 of 135.6(2)° indicates that the phenyl group is less rotated away from the ligand plane in comparison to its coordinated form pointing to a small rotational barrier.

Catalysis. Complex **2** was tested as catalyst for olefin epoxidation of *cis*-cyclooctene as shown in eq 1. Typically, 2.7 mmol of the substrate were dissolved in 5 mL of chloroform that contained 2.7 mmol of dibutyl ether as

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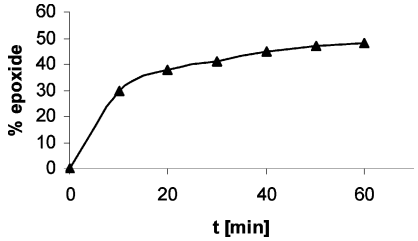
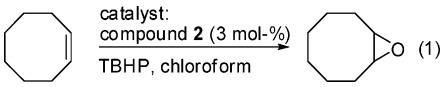


Figure 5. Reaction progress of the olefin epoxidation of *cis*-cyclooctene using complex **2** as a catalyst.

internal standard and catalytic amounts of **2** (3 mol-% vs the olefin).



This solution was heated to 50 °C and treated with a solution of *tert*-butylhydroperoxide (TBHP) in *n*-decane (1.5-fold excess), which was added at once. After addition of the peroxide a color change from green to brown-red was apparent. The oxidation was monitored by GC-MS. Aliquots were taken every 10 min, treated with MnO_2 to destroy unreacted peroxide, filtered over Celite, and analyzed. The reaction progress is given in Figure 5 showing fast conversion up to approximately 45%, after which the rate decreases dramatically and reaches a plateau at approximately 50%. The GC-MS spectra revealed a clean catalytic reaction because no other reaction or decomposition products could be detected. In particular, 2-*tert*-butoxycyclooctanol is absent, a possible side product resulting from ring opening of the epoxide by nucleophilic attack of the formed *tert*-butanol. In addition, it is interesting to note that no induction period was detected in contrast to similar rhenium(V) complexes that contain salen-based ligands.[9] However, the catalytic performance of compound **2** is not comparable to the that of, for example, MTO.[55,56] Whether the mechanism involves a Re(VII) or a Re(V) species is unclear because we were not able to isolate any pure rhenium compounds after the epoxidation reactions. Herrmann and co-workers have convincingly shown that the catalytically active species in epoxidations with MTO involves the 7-coordinate bisperoxo rhenium(VII) complex $[ReO_2(O_2)_2(H_2O)]$.[18] In contrast, the catalytically active species in the few epoxidations involving other than rhenium(VII) compounds is less clear, but oxidation to a rhenium(VII) peroxo species is suggested.[9,26] Thus, for the formation of the active catalyst, **2** is presumably oxidized to the putative $[ReO(O_2)Cl_2(DPO)]$ under oxidation of the phosphine ligand and forming a vacant coordination site for the peroxide unit. Less likely is the dissociation of chlorine atoms, which is supported by the fact the anionic complexes **3**, **4**, and **5** do not show any catalytic activity under these conditions.

Under the same conditions, complex **2** was tested as catalyst in the epoxidation of styrene with TBHP, but no oxidation was observed. We assume that during catalysis, the catalyst decomposed before conversion of the substrate indicated by the disappearance of the green color. Application of similar rhenium(V) complexes with modified ligands are currently under investigation with the aim to improve the stability and efficiency of the catalyst.

Conclusion

We showed that mononuclear complexes of the type $[ReOLCl_2(PPh_3)]$ or $[NBu_4][ReOLCl_3]$, where L represents acetylacetone derived β-ketoamine ligands, can be prepared in high yields. All compounds coordinate to the rhenium center with the oxygen atom of the ligands *trans* to the Re═O group. The two chlorine atoms occupy *trans* positions to each other in contrast to other compounds of this type. A surprising finding is the fact that no complexes of the type $[ReOL_2Cl]$ could be obtained, independent of the steric bulk imposed by the ligands and the number of coordinating atoms emphasizing their unique electronic features in comparison to salicylaldehyde derived ligands. Compound **2** proved to be a catalyst for the epoxidation of *cis*-cyclooctene with *tert*-butylhydroperoxide at 50 °C. It must be noted that these catalytic reactions are very clean because the epoxide is the only detectable product. The initial reaction rate is high without the occurrence of an induction period in contrast to salicylaldehyde-based rhenium complexes.[9] However, the catalytic activity is low in comparison to rhenium(VII) systems, and the compounds proved to be inactive toward more challenging substrates such as styrene.[56]

Acknowledgment. We are grateful to the Deutsche Forschungsgemeinschaft for generous support of this work (MO 963/2). We thank Mr. Nebel for his assistance in measuring the GC-MS spectra.

Supporting Information Available: X-ray crystallographic data in standard CIF format for compounds **1**, **2**, **4**, **5**, and MTPOH. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data (excluding structure factors) for the structures have been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publications CCCD 637542 (**1**), 636365 (**2**), 636366 (**4**), 636367 (**5**), and 637543 (MTPOH). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, U.K. (fax: +(44)1223−336-033; email: deposit@ccdc.cam.ac.uk).

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