Synthesis, Structure, and Catalytic Reactivity of N,N,S- and O,N,S-Tridentate Oxorhenium(V) Complexes

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Introduction

Methyltrioxorhenium(VII) (CH_3ReO_3 or MTO) has been known for about 20 years,[1] and with the availability of more convenient methods for its preparation,[2] its catalytic properties have been extensively studied.[3−5] We have reported that MTO reacts with 2-(mercaptomethyl)thiophenol, *o*-$HSC_6H_4CH_2SH$ or H_2mtp, to form complexes in which mtp acts as a bidentate thiolate ligand.[6] This series of compounds has the formula MeReO(mtp)L, in which L is a pyridine, phosphine, sulfide, etc. They are proving to be effective catalysts for oxygen-transfer reactions, such as that from PyO to PPh_3.[7] In the course of our work three new compounds, **1**−**3**, containing tridentate ligands having NNS and ONS donor sets were prepared, characterized, and tested for catalytic activity. The structural formulas of **1**−**3** are given in Chart 1.

Compound **1** was obtained from $(Bu_4N)[ReOCl_4]$[8] and 2-(2-pyridyl)benzothiazoline. This ligand has the form $\mathbf{HL_2}$ in the solid state, but in chloroform solution[9] it exists in equilibrium with $\mathbf{HL_1}$, see Chart 2. The reaction occurring is

$$\mathbf{HL^1} + (Bu_4N)[ReOCl_4] \rightarrow \mathbf{L_1}ReOCl_2 + (Bu_4N)Cl + HCl \quad (1)$$

The same ligand, in reaction with MTO, undergoes reduction of the imine bond to yield a new ligand $\mathbf{HL^4}$ as **2** forms. The reaction requires a 1:3 MTO:$\mathbf{HL^1}$ stoichiometry in chloroform, with 2 mol of a new compound, $\mathbf{L^5}$, formed according to this equation,

$$CH_3ReO_3 + 3\mathbf{HL^1} \rightarrow \underset{\mathbf{2}}{CH_3ReOL^4} + 2\mathbf{L^5} + 2H_2O \quad (2)$$

Compound **3** was prepared from MTO and 2-(2-hydroxyphenol)benzothiazoline, $\mathbf{HL^3}$. All three compounds gave elemental analyses that agreed with the reported compositions, as summarized in the Experimental Section. The ^1H NMR spectrum of **2** shows the two inequivalent hydrogen atoms on the one carbon atom of $\mathbf{L^4}$; they couple with one another, forming a pair of doublets around 4.7 and 6.0 ppm. The use of $^1H-^{13}C$ COSY NMR spectroscopy confirmed this assignment. The ^{13}C NMR spectrum of **2** shows 13 peaks, of which that at 68.13 ppm can be assigned to the methylene carbon and that at 6.00 ppm to Re−CH_3.

Chart 1. Structural Formulas of Three New Oxorhenium(V) Compounds with Tridentate Ligands

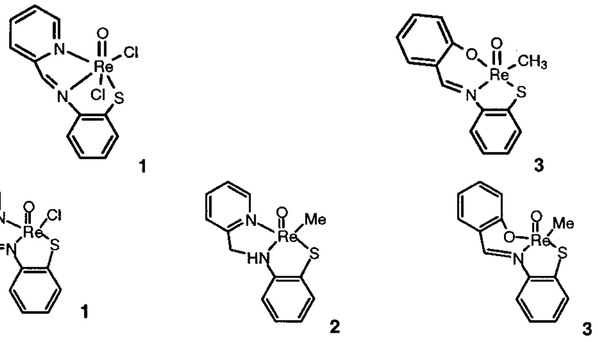
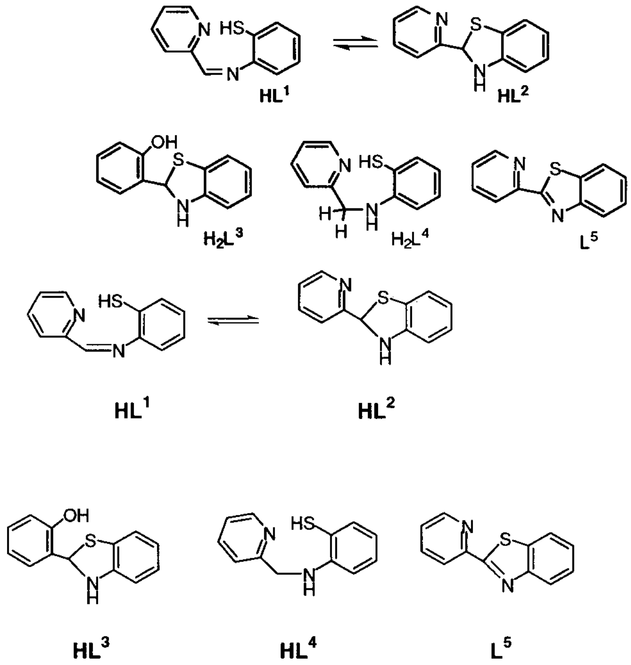


Chart 2. Ligands Used in Starting Materials and Found in Products



Compound **2** was further characterized by X-ray crystallography, owing to the unusual ligand reduction reaction in its formation. As shown in Figure 1, the diffraction study confirms the structure of the new ligand and the five-coordinate geometry about rhenium. Important distances and angles are given in Table 1. We note these in particular: (a) *d*(Re−CH_3) = 213.5(5) pm and *d*(Re−O) = 168.4(3) pm, comparable to those in MeReO(mtp)−PPh_3, 212.5 and 167.7 pm;[6] (b) *d*(Re−S) = 227.9(1) pm, as compared to 232.9 pm for the *phenolic* Re−S bond in the same reference compound and 229.9 pm in $\{MeReO(mtp)\}_2$;[6] (c) *d*(Re−N) 198.4(4) pm for the amido nitrogen and 211.5(4) pm for the pyridine nitrogen emphasize the covalent nature of the one bond and the coordinate nature of the other;[10] (d) a sum of bond angles about the amido nitrogen of 359.6°, supporting sp^2 hybridization of this atom.

All three Re(V) complexes (at a concentration of 1% of substrate) catalyze the transfer of an oxygen atom from pyridine

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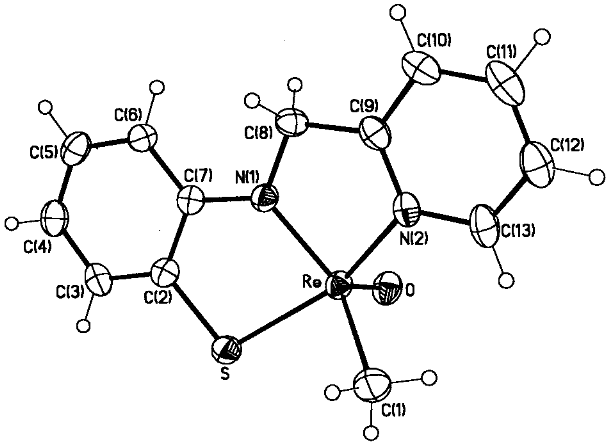

Figure 1. ORTEP drawing of the structure of **2** in which ellipsoids are drawn at the 50% probability level.

N-oxide to tris(*p*-methylphenyl)phosphine; **2** and **3** are most effective. Within 1.5 days, the reaction was complete with these catalysts; the reaction progress was monitored using ^{1}H NMR. The strong doublet at δ 8.1 can be assigned to the H atoms on the carbon bonded to N of PyO; it gradually decreased in intensity. Concurrently, a new doublet at δ 8.5 increased; it is attributed to the two H atoms on the carbon bonded to N of pyridine.

With **1** as the catalyst, on the other hand, some pyridine oxide remained in the solution at that time. Pyridine *N*-oxide must access the primary coordination sphere of rhenium, which would be expected to be more difficult for **1** given that it is six-coordinate. It may be, although this has not been proved, that a dioxorhenium(VII) intermediate lies on the reaction coordinate. The prospect of identifying this and perhaps other intermediates in the system remains a matter of interest to us. Compound **2** does not react with PPh$_3$, but it does react with pyridine *N*-oxides. When a 20-fold excess of 4-methylpyridine *N*-oxide was added to a solution of **2** in chloroform, its color changed from brown to wine-red. A new ^{1}H NMR resonance appeared at 5.8 ppm; 3 h later no resonances were seen in the range 4.0−6.5 ppm. Two new doublets appeared at 7.3 and 8.4 ppm from the 4-methylpyridine that was formed. These findings suggest that **2** has been oxidized by PyO. With an excess of the pyridine oxide, the ligand of **2** would itself be oxidized, accounting for the disappearance from the ^{1}H NMR spectrum of the doublets of the methylene group.

Experimental Section

General. (Bu^{n}N$_4$)[ReOCl$_4$] was prepared and purified according to the literature.[8] Other chemicals and solvents were reagent-grade materials and used without further purification. The ^{1}H NMR spectra were recorded on a Varian spectrometer at 300 MHz. COSY ^{1}H−^{13}C NMR spectra were determined with a Bruker 400 spectrometer.

Ligands. (a) Ligand **HL^1** (and thus **HL^2**) was prepared from 2-(pyridine)carboxyaldehyde (0.96 mL, 10 mmol, 99%) and 2-aminothiophenol (1.19 mL, 10 mmol, 99%) in 40 mL of dry EtOH. Oxygen was purged from the solution with a stream of argon, and the mixture was then heated to 80 °C for 4 h. The solvent was then removed under reduced pressure. The material so obtained was then dissolved in 20 mL of chloroform; olive-colored crystals were obtained by layering the solution with 20 mL of hexane. Yield of 2-(2-pyridyl)benzothiazoline: 95%. ^{1}H NMR in methanol-d_4: δ 6.26 (s, 1H, =CH−S), 6.62 (m, 2H, Ph), 6.88 (m, 2H, Ph), 7.22 (m, 1H, 5-H of Py), 7.60 (d, 1H, 3-H of Py), 7.74 (d, 1H, 4-H of Py), and 8.37 (m, 1H, 6-H of Py).

(b) **HL^3** was prepared by refluxing salicylaldehyde with an equimolar amount of 2-aminothiophenol in ethanol under argon. The ^{1}H NMR spectrum in methanol-d_4 showed these resonances: δ 6.56 (s, CH$_2$−S), 6.67 (m, 2H), 6.78 (m, 2H), 6.90 (m, 2H) 7.10 (m, 1H), and 7.46 (m, 1H) for the aromatic protons.

Table 1. Selected Bond Lengths (pm) and Angles (deg) for **2**

	Distances		
Re−O	168.4(3)	S−C(2)	176.5(5)
Re−N(1)	198.4(4)	N(1)−C(7)	138.8(6)
Re−N(2)	211.5(4)	N(1)−C(7)	145.3(6)
Re−C(1)	213.5(5)	N(1)−C(8)	134.4(6)
Re−S	227.9(1)		
	Angles		
O−Re−N(1)	119.83(17)	C(1)−Re−S	84.73(15)
O−Re−N(2)	106.58(16)	C(2)−S−Re	99.93(16)
N(1)−Re−N(2)	77.39(16)	C(7)−N(1)−C(8)	117.7(4)
O−Re−C(1)	110.6(2)	C(7)−N(1)−Re	122.0(3)
N(1)−Re−C(1)	129.57(19)	C(8)−N(1)−Re	119.9(3)
N(2)−Re−C(1)	87.42(19)	C(13)−N(2)−C(9)	118.8(4)
O−Re−S	108.26(12)	C(13)−N(2)−C(9)	125.0(4)
N(1)−Re−S	81.50	C(9)−N(2)−Re	115.7(3)
N(2)−Re−S	144.85(11)		

Table 2. Crystallographic Data for **2**

chem formula	$C_{13}H_{13}N_2OReS$	space group	$P2_1/n$
fw	431.51	T	173(2) K
a	7.2770(5) Å	λ	0.71073 Å
b	12.6460(9) Å	ρ_{calcd}	2.238 g cm^{-3}
c	13.9716(9) Å	μ	9.639 mm^{-1}
α, β, γ	90°, 95.070(1)°, 90°	R1 ($I > 2\sigma(I), F_o^2$)[a]	0.0244
V	1280.71(15) Å^3	wR2 ($I > 2\sigma(I), F_o^2$)[a]	0.0598
Z	4		

[a] Quantity minimized: $R(wF^2) = \sum[w(F_o^2 - F_c^2)]/\sum[(wF_o^2)^2]^{1/2}$; $R = \sum\Delta/\sum(F_o)$, $\Delta = |(F_o - F_c)|$.

Rhenium Complexes. (a) **L^1**ReOCl$_2$, **1**, was prepared from (Bu^{n}N$_4$)-[ReOCl$_4$] (5.86 g, 10 mmol) and **HL^2** (2.14 g, 10 mmol) in 20 mL of dichloromethane. After stirring for 30 min at room temperature, a brown solid formed, which was filtered. Yield of **1**: 85%. ^{1}H NMR in methanol-d_4: δ 6.52 (s), 6.85 (t), 6.96 (t), 7.50 (m, 4H, Ph), 7.98 (m), 8.06 (d), 8.37 (m, 4H, Py), and 9.81 (d, 1H, −N=CH=). Anal. Calcd for ReC$_{12}$H$_9$Cl$_2$ON$_2$S: C, 29.63; H, 1.86; N, 5.76. Found: C, 29.47; H, 1.94; N 5.57.

(b) MeReO**L^4**, **2**, was obtained by filtration as a brown solid that precipitated from MeReO$_3$ (2.49 g, 10 mmol) and **HL^2** (6.42 g, 30 mmol) that were stirred for 1 h in 30 mL of dichloromethane. Yield: 80%. X-ray quality crystals were obtained by recrystallization from the same solvent. ^{1}H NMR: δ 2.92 (s, 3H, CH$_3$−Re), 4.76 (d), 6.05 (d, 2H, −CH$_2$−), 7.00 (m), 7.12 (m, 4H, Ph), 7.77 (m), 8.15 (m), 9.43 (d, 4H, Py). ^{13}C NMR: δ 5.99 (CH$_3$−Re), 68.12 (−CH$_2$−), 111.67, 120.46, 120.94. 124.94, 125.08, 128.61, 141.93, 145.89, 152.20, 159.63, 173.89. Anal. Calcd for ReC$_{12}$H$_{13}$ONS: C, 36.18; H, 3.04; N, 6.49. Found: C, 35.31; H, 3.08; N, 6.17.

X-ray Crystallography. A crystal with approximate dimensions 0.4 × 0.3 × 0.2 mm was selected under ambient conditions and attached to the tip of a glass capillary. The crystal was mounted in a stream of cold nitrogen at 173(2) K and centered in the X-ray beam by using a video camera. The crystal evaluation and data collection were performed on a Bruker CCD-1000 diffractometer with Mo Kα (λ = 0.71073 Å) radiation. A successful solution by the direct method located most of the non-hydrogen atoms. The remaining non-hydrogen atoms were located in an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms were included in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients. Details of the structure solution are presented in Table 2.

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Supporting Information Available: NMR data and COSY figures and a crystallographic file in CIF format for the structure determination of **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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