Rhenium(V)−Salen Complexes: Configurational Control and Ligand Exchange

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Reactions of $ReO(PPh_3)_2Cl_3$ with tetradentate bis(salicylideneamine) ligands, H_2salpd (**1**) and H_2salbd (**2**), in different alcohols gave the novel mixed-ligand rhenium complexes ReO(sal)OAlk (OAlk = variety of alkoxy ligands). Configurational studies show that the rhenium complexes ReO(salpd)OAlk (**1a**−**f**) display either a symmetrical or a nonsymmetrical configuration, depending on the size of the alcohol and its boiling point. The rhenium complexes ReO(salbd)OAlk (**2a**−**d**) are all nonsymmetrical due to the number of carbons that bridge the imine nitrogens. In the case of the symmetrical ReO(salpd)OMe (**1a**) complex the methoxy ligand can be exchanged for a number of ligands of different types (OAlk, OPh, SAlk, OC(O)Alk). In the newly formed complexes the original configuration was retained except for the ReO(salpd)SAlk (**1i,j**) complexes which were isolated in the nonsymmetrical configuration. Starting from the nonsymmetrical ReO(salpd)OPr (**2c**) complex, ligand exchange led to a mixture of the symmetrical and nonsymmetrical complexes, with ratios depending on the reaction time. The crystal structures of ReO(salbd)OPr (**2c**), and ReO(salpd)OPhOMe (**1g**) have been determined. ReO(salbd)OPr crystallizes in the triclinic space group $P\bar{1}$, $Z = 2$, with $a = 10.0344(16)$ Å, $b = 10.647(2)$ Å, $c = 11.481(2)$ Å, $\alpha = 86.551(15)°$, $\beta = 86.998(14)°$, $\gamma = 80.112(15)°$, $V = 1205.1(4)$ Å^3, and final $R = 0.0460$. Crystals of ReO(salpd)OPhOMe are orthorhombic, space group $P2_12_12_1$, $Z = 4$, with $a = 10.6222(15)$ Å, $b = 12.442(3)$ Å, $c = 16.354(3)$ Å, $V = 2161.4(7)$ Å^3, and final $R = 0.0371$. Under the influence of traces of water a number of symmetrical complexes react to a "dimeric" structure, consisting of two ReO(salpd) moieties bridged by an oxygen atom with the bridging Re−O−Re angle symmetrically imposed at 180°. $[ReO(salpd)]_2O$ (**3**) crystallizes in the monoclinic, space group $P2_1/c$, $Z = 4$, with $a = 14.860(2)$ Å, $b = 12.545(2)$ Å, $c = 16.5111(17)$ Å, $\beta = 95.030(10)°$, $V = 3066.1(7)$ Å^3, and final $R = 0.0439$.

Introduction

Rhenium complexes with Schiff base ligands derived from salicylaldehyde and diamines (salenes) have received attention for various reasons.[1−6] Rhenium is widely used as a nonradioactive model for technetium, which is used in nuclear medicine. However, rhenium itself also has potential to serve as a nuclide in radiotherapy[7] since its isotopes ^{186}Re and ^{188}Re emit β radiation.

The first Schiff base rhenium complexes were reported by Middleton *et al.* in 1979.[1] The well-known *O,N,N,O*-tetradentate Schiff base ligands can theoretically adopt four different configurations, as depicted in the structures A−D in Chart 1.[8] However, due to poor solubility of the complexes their characterization has relied mainly on infrared spectroscopy, mass spectrometry, and elemental analysis, and therefore, the geometry of the Schiff base ligand has not been studied extensively.

Although it has been stated that ligands with less than five atoms between the two imine nitrogens lead to a configuration in which the ligand lies in the equatorial plane with respect to the Re═O moiety (i.e. configuration A),[6] Herrmann *et al.* recently reported that this configuration has frequently been incorrectly assigned to such complexes.[8] However, extensive configurational studies have not yet been performed.[9,10]

This paper describes the synthesis and characterization of a novel type of *O,N,N,O*-tetradentate Schiff base mixed-ligand rhenium complexes that are well soluble in organic solvents. For the first time two different configurations of one complex have been synthesized via two independent pathways. A thermally induced rearrangement from type A into B has been

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(10) The effect of chain length of the related Schiff-base ligand *N,N*′-ethylenebis(((1-hydroxy-2-naphthyl)methylene)amine) (H_2napen) on the coordination chemistry of cobalt(II) has been studied: Ashmawy, F. M.; Issa, R. M.; Amer, S. A.; McAuliffe, C. A.; Parish, R. V. *J. Chem. Soc., Dalton Trans.* **1986**, 421.

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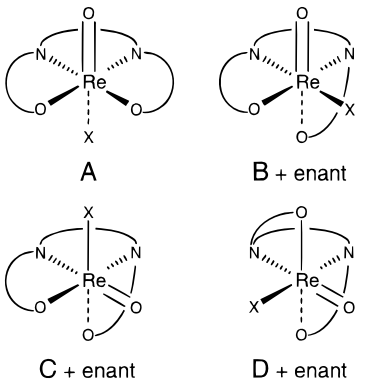
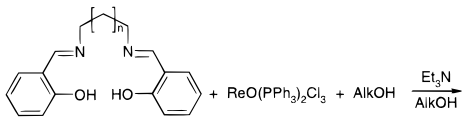
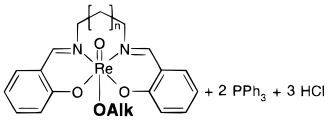
Chart 1. Possible Configurations for *O*,*N*,*N*,*O*-Tetradentate Schiff Base Ligands



Scheme 1. Structures of Complexes Directly Synthesized in Different Alcohols



1, n = 1 (**H$_2$salpd**)
2, n = 2 (**H$_2$salbd**)



n = 1; **1a**: OAlk = OMe, **1b**: OAlk = OEt, **1c**: OAlk = OPr, **1d**: OAlk = OBu, **1e**: OAlk = O*i*Pr, **1f**: OAlk = O*t*Bu
n = 2; **2a**: OAlk = OMe, **2b**: OAlk = OEt, **2c**: OAlk = OPr, **2d**: OAlk = O*i*Pr

studied using NMR spectroscopy. The monodentate ligand (X in Chart 1) has been exchanged quantitatively for a variety of other ligands, demonstrating the potential of this system for the linkage of biomolecules directly to the rhenium core. Furthermore, the consequences of the ligand exchange for the complex structure have been investigated.

Results and Discussion

Direct Complex Formation. Novel mixed-ligand rhenium(V) complexes containing a variety of alkoxy ligands were synthesized by reaction of the ligands H_2salpd (**1**) and H_2salbd (**2**), containing three- and four-carbon alkyl chains that bridge the imino groups, respectively, with $ReO(PPh_3)_2Cl_3$ in different alcohols as a solvent (Scheme 1).

All reactions were carried out in the presence of triethylamine as a base, and instead of giving the chloro complexes ReO(sal)Cl, this surprisingly resulted in the formation of the alkoxy complexes ReO(sal)OAlk in yields of 35−45%. The formation of a salen−alkoxy complex has not been observed before. Previously, Tisato *et al.*[6] reported the formation of the corresponding chloro complex, starting from sal$_2$en ligands with 5-, 6- and 7-carbon alkyl chains that bridge the imino groups.[11]

The formation of the alkoxy complexes is clearly proven by ^{1}H NMR spectroscopy. The signals for the Re−OCH$_n$ hydrogen atoms in the complexes appeared at positions ranging from 2.0 ppm downfield (complex **1e**: Re−OC*H*$(CH_3)_2$, 5.99 ppm; HOC*H*$(CH_3)_2$, 4.04 ppm) to 0.3 ppm upfield (complex **1b**: Re−OCH_2CH$_3$, 3.39 ppm; HOCH_2CH$_3$, 3.72 ppm) compared to the signals of the OCH$_n$ hydrogens in the free alcohol.

Table 1. Configurations and Imine Hydrogen Shifts of Complexes Directly Synthesized in Different Alcohols

complex	alkoxy ligand	salpd	$\delta_{CH=N}$ (ppm)	salbd	$\delta_{CH=N}$ (ppm)
			Linear		
1a/**2a**	OMe	sym	8.09	nonsym	7.99/7.40
1b/**2b**	OEt	sym	8.05	nonsym	7.98/7.40
1c/**2c**	OPr	nonsym	7.60/7.13	nonsym	7.98/7.40
1d/-	OBu	nonsym	7.60/7.12	not isolated	
			Branched		
1e/**2d**	O*i*Pr	nonsym	7.53/7.10	nonsym	7.95/7.41
1f/**2e**	O*t*Bu	sym	7.95	Cl complex	8.05/7.65

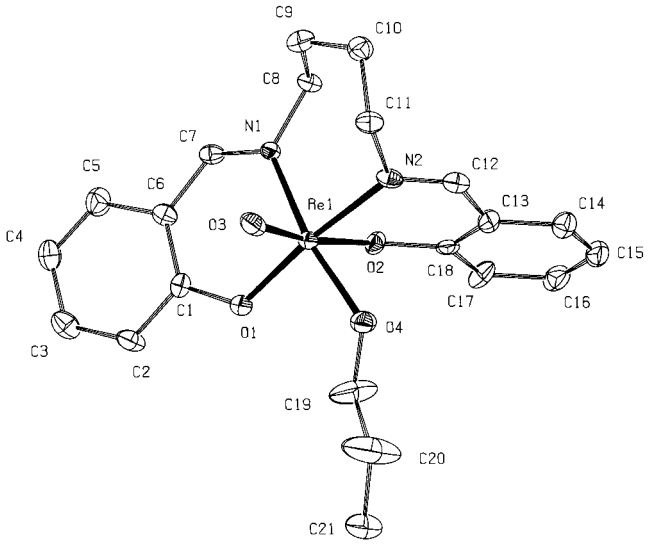


Figure 1. Atomic displacement ellipsoid plot[20] of ReO(salbd)OPr (**2c**) drawn at the 50% probability level. Hydrogen atoms and the solvate molecule have been omitted for clarity.

Compared to the chloro complexes, the alkoxy complexes are much more soluble, which facilitates (configurational) characterization using NMR techniques. The complexes were characterized by ^{1}H NMR, ^{13}C NMR, FAB-MS, and elemental analysis,[12] and in addition for a number of complexes single-crystal X-ray structure analyses were performed (*vide infra*).

The configurations (symmetric or nonsymmetric) of the different alkoxy complexes were assigned on the basis of their ^{1}H NMR spectra; all hydrogen atoms of a nonsymmetrical product are in different chemical environments, whereas those of a symmetrical product are not. Table 1 lists the chemical shifts for the imine hydrogens and the configurations of the complexes. This clearly shows that tetradentate *O*,*N*,*N*,*O* Schiff base H_2salpd (**1**) forms nonsymmetrical complexes (type B) as well as symmetrical complexes (type A) and that H_2salbd (**2**) exclusively forms nonsymmetrical complexes. X-ray crystal structures of ReO(salbd)OPr (**2c**, Figure 1) and ReO(salbd)-O*i*Pr[13] (**2d**; see Supporting Information) confirm the structural type B. The two halves of the salbd ligand are in perpendicular planes with one *N*,*O*-unit of B located in the equatorial plane and the phenolate oxygen atom of the other *N*,*O*-unit being *trans*

(11) Tisato *et al.*[6] used $[NBu_4][ReOCl_4]$ instead of $ReO(PPh_3)_2Cl_3$; however, this would not explain the formation of the chloro over the alkoxy complex, since chloro ligands are present in both rhenium starting materials.

(12) A satisfactory elemental analysis could not be obtained of all complexes, although they had been characterized using NMR, TLC, and in one case even X-ray crystallography.

(13) There are no significant differences in the overall conformation of the ReO(salbd) moieties of **2c**,**d**.

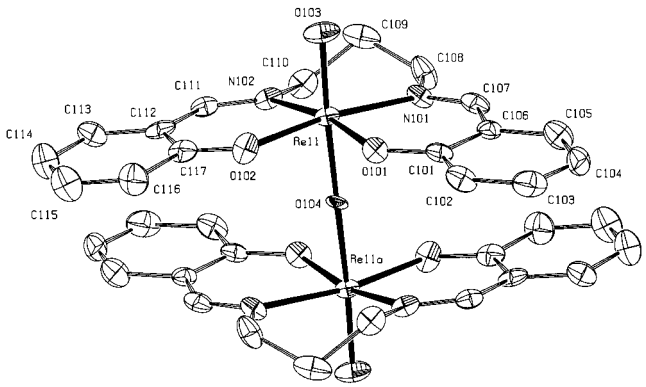


Figure 2. Atomic displacement ellipsoid plot[20] of $[ReO(salpd)]_2O$ (**3**) drawn at the 50% probability level. Only the molecule located at the $(0, {}^1/_2, 0)$ inversion center is shown. Hydrogen atoms have been omitted for clarity.

to the Re═O moiety. The acute angle between the planes through the *N*,*O*-units amounts to 74.6(2) and 72.1(2)° for ReO(salbd)OPr (**2c**) and ReO(salbd)O*i*Pr (**2d**), respectively. The asymmetric unit of ReO(salbd)OPr (**2c**) contains a chloroform solvate molecule, which is linked to the atoms O1 and O3 of the Re complex *via* a bifurcated C−H···O hydrogen bond.

Recrystallization of the symmetrical complexes from a variety of solvents gave crystals of the complex $[ReO(salpd)]_2O$ (**3**, Figure 2) in which the two alkoxy ligands had been replaced by a μ-oxygen atom.[14] The formation of the μ-oxo bond probably occurs because the alkoxy moieties exchange with water from the air, after which they dimerize with elimination of a water molecule (eq 1), similar to the reaction found for

$$O{=}Re(sal){-}OAlk + H_2O \rightarrow O{=}Re(sal){-}OH + AlkOH \quad (1a)$$

$$2\ O{=}Re(sal){-}OH \rightarrow O{=}Re(sal){-}O{-}(sal)Re{=}O + H_2O \quad (1b)$$

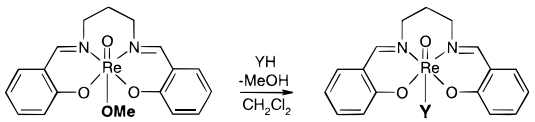
oxorhenium porphyrins.[15] Since for the formation of this type of μ-oxo complexes both halves need to be symmetrical, probably the complexes based on H_2salbd (**2**) cannot give this type of complexes.

In the X-ray crystal structure the asymmetric unit of $[ReO(salpd)]_2O$ (**3**) contains two unique half-molecules, with the bridging oxygen atoms located at a crystallographic inversion center. The molecular conformation and crystal packing are essentially equal to those of the corresponding technetium compound.[2]

All complexes of ligand H_2salbd (**2**), in which four carbon atoms bridge the imino nitrogens, are nonsymmetrical (structural type B in Chart 1). Attempts to build CPK molecular models of their symmetrical isomers show that this particular bridge length prevents the formation of symmetrical complexes.

In the case of the ligand H_2salpd (**1**), the complex configuration depends on a number of factors. It is known that, due to the *trans* influence of the Re═O bond, the binding of a hard atom ($RO^- > Cl^-$, $Br^- > R_3N$) *trans* to the Re═O group is preferred.[4,8] In rhenium−salen complexes bearing a halogen as a ligand this results in complexes with configuration B as was shown by Herrmann *et al.*[8] However, the complexes in

Scheme 2. Structures of Complexes Synthesized via Ligand Exchange



1c: Y = OPr, **1g**: Y = O-C_4H_4-*p*OMe, **1h**: Y = OAc, **1i**: Y = SEt, **1j**: Y = SPr, **1k**: Y = OChol

Table 1 *all* possess a trans RO^- group (R = aryl or alkyl), which indicates that this factor is of less importance here. Since the complex formations have been performed at different temperatures, determined by the boiling point of the concerning alcohol, this may explain the observed trend in the configurational outcome for the complexes with linear alkoxy ligands. The configuration of the complex changed on going from ethanol (bp 78 °C) to 1-propanol (bp 97 °C) giving in the latter case the thermodynamically more stable, nonsymmetric product as a result of the higher reaction temperature.[16] Due to the linearity of the alkoxy ligands it seems possible that steric factors can be neglected in explaining the observed trend.

The explanation for the configuration of the complexes with the branched alcohols is more complicated. The configurations cannot be explained by simply taking into account the reaction temperature. Here steric factors are likely to play a more important role, as follows from the formation of the complexes ReO(salpd)O*i*Pr and ReO(salpd)O*t*Bu (**1e**,**f**, Table 1). The complex ReO(salpd)O*i*Pr (**1e**) (bp *i*-PrOH 82 °C) is formed at nearly the same temperature as ReO(salpd)OEt (**1b**) (bp EtOH 78 °C). However, the first complex has a nonsymmetrical configuration, whereas ReO(salpd)OEt (**1b**) is symmetrical.

In the case of ReO(salpd)OtBu (**1f**), the reaction temperature should enable the formation of the nonsymmetrical (thermodynamic) product, but due to the bulkiness of the *tert*-butoxy group this is not possible and the symmetrical product is formed. In the case of the ligand H_2salbd (**2**), the nonsymmetrical complex ReO(salbd)Cl (**2e**) was isolated. This was confirmed by the ^{1}H NMR spectrum, which did not exhibit the presence of any alkoxy ligand, whereas it did show that the salen moiety was in a nonsymmetrical configuration. Furthermore FAB-MS gave a peak at *m*/*z* 531.9 with the correct Re−Cl pattern, corresponding to the ReO(salbd)Cl (**2e**) complex. This confirms the observation based on CPK molecular modeling that the rhenium complexes based on ligand H_2salbd (**2**) can only be nonsymmetrical.

Complex Formation via Ligand Exchange. To study whether a complex would retain its configuration upon alkoxy ligand exchange, the methoxy moiety was exchanged for a number of other ligands. Therefore the symmetrical methoxy complex ReO(salpd)OMe (**1a**) was refluxed in CH_2Cl_2 in the presence of an excess of ligand (Y), the methanol being trapped using 4 Å molecular sieves (Scheme 2). The boiling point of CH_2Cl_2 is insufficient to facilitate "reorganization" to the (nonsymmetric) thermodynamic product.

This synthesis provided an indirect route for the preparation of the symmetrical ReO(salpd)OPr (**1c**) complex. ^{1}H NMR data clearly show the symmetry of the complex, and no traces of the methoxy complex were observed. While for the nonsymmetrical propoxy complex (prepared via the direct route) the signals for the OCH_2 hydrogen atoms give rise to multiplets at

(14) Very recently μ-oxo-bridged complex formation from a ReO(L)−OMe complex has also been observed: Reisgys, M.; Spies, H.; Johannsen, B.; Leibnitz, P.; Pietzsch, H.-J. *Chem. Ber./Recueil* **1997**, *130*, 1343.

(15) Buchler, J. W.; Kruppa, S. B. *Z. Naturforsch.* **1990**, *45b*, 518.

(16) On the basis of the configuration of $ReOCl(NO)_2$ complexes, Tisato *et al.*[6] postulated that the nonsymmetrical configuration is thermodynamically more stable.

Table 2. Configurations and Imine Hydrogen Shifts of Complexes Synthesized via Ligand Exchange

complex	Y	sym/nonsym	$\delta_{CH=N}$ (ppm)
1c	OPr	sym	7.99
1g	OC_6H_4-*p*OMe	sym	8.15
1h	OAc	sym	8.00
1i	SEt	nonsym	8.06/7.80
1j	SPr	nonsym	8.00/7.74
1k	OChol[a]	sym	8.03/8.00[b]

[a] OChol = cholesteroxy. [b] Two CH=N signals could be observed due to the chirality of the cholesterol ligand; however, the complex is symmetrical.

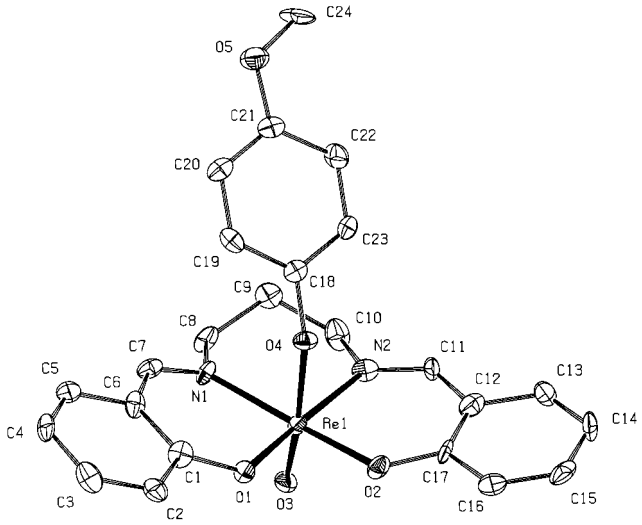


Figure 3. Atomic displacement ellipsoid plot[20] of ReO(salpd)OPhOMe (**1g**) drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity.

5.4 and 4.8 ppm, the OCH_2 hydrogens of the symmetrical complex give a triplet at 3.16 ppm (the OCH_2 hydrogens of 1-propanol give a triplet at 3.54 ppm).

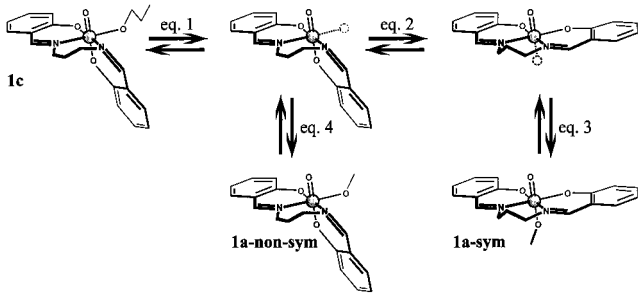
In addition to alkoxy ligands a number of different ligands, summarized in Table 2, were linked via this "methoxy exchange route".

Exchanging the methoxy for a *p*-methoxyphenoxy ligand resulted in a complex with preserved symmetry (**1g**, Table 2). Since the hardness of the *p*-methoxyphenoxy ligand is very close to that of the salen−phenoxy moiety no structural rearrangements, caused by the *trans* effect, were expected. X-ray structure analysis confirms the preservation of symmetry. The acute angle between the least-squares planes through the *N*,*O*-units of ReO(salpd)OPhOMe (**1g**) amounts to 29.9(2)° (Figure 3), which is in between the values observed for $[ReO(salpd)]_2O$ (**3**) (5.8(2) and 8.3(2)° for the two independent molecules) and for TcO(salpd)Cl (43°).[2]

The substitution of an alkoxy for a carboxy ligand gave the acetate complex (**1h**, Table 2), again in the symmetrical configuration since the acetate oxygen is a "hard" center. Introduction of thiolate ligands (**1i**,**j**, Table 2) resulted in a change of configuration. Since the thiols resemble the corresponding alcohols in shape, this change can be fully attributed to the *trans* effect, which does not allow a soft sulfur to bind *trans* to the Re=O moiety (vide supra).

To study whether this type of ligand exchange could also be used for the linkage of large biomolecules directly onto the rhenium core, a cholesteroxy ligand was introduced (**1k**, Table 2). The ^{1}H NMR spectrum clearly shows configurational preservation, which could be expected on the grounds of the *trans* effect, as well as steric factors which do not allow the formation of the nonsymmetrical complex.

Scheme 3. Proposed Mode of Rearrangement from nonsymmetric ReO(salpd)OPr (**1c**) to symmetric and nonsymmetric Re(salpd)OMe (**1a**)



In all ligand exchange reactions the conversion was essentially quantitative and no traces of the starting complex could be observed by NMR spectroscopy. Furthermore, the ease of purification, which in most cases consists of removing the solvent and excess ligand Y under reduced pressure, makes this a very effective method for the synthesis of a large variety of complexes.

Ligand exchange has also been carried out with the nonsymmetrical ReO(salpd)OPr (**1c**, Scheme 3) by refluxing in CH_2Cl_2 in the presence of a large excess of MeOH. After 1 day the ^{1}H NMR spectrum showed that 30% of the starting complex had been converted into the symmetrical methoxy complex (**1a-sym**). After 10 days the ^{1}H NMR spectrum exhibited no starting material signals but instead showed 78% of the symmetrical methoxy complex (**1a-sym**) and 22% of the nonsymmetrical methoxy complex (**1a-non-sym**). After 14 days the ratio **1a-sym**:**1a-non-sym** had changed to 69:31. These observations suggest the mechanism shown in Scheme 3.

The complex first loses its propoxy ligand leaving a vacancy on the rhenium core (equilibrium 1). The complex then rearranges (equilibrium 2) to the symmetrical complex. The methanol, which is present in large excess, subsequently binds to the rhenium core (equilibrium 3) to form the symmetrical methoxy complex **1a-sym**. However, via reversal of the last two steps the symmetrical complex **1a-sym** can be transformed into the nonsymmetrical complex possessing a vacancy, which can bind a methoxy ligand (equilibrium 4), resulting in formation of the nonsymmetrical methoxy complex **1a-sym**.[17]

X-ray Crystal Structures. In the case of ReO(salpd)O-PhOMe (**1g**), ReO(salbd)OPr (**2c**), and $[ReO(salpd)]_2O$ (**3**) crystals suitable for single-crystal X-ray structure analyses were obtained after recrystallization from $CDCl_3$. In the case of ReO(salbd)-O*i*Pr (**2d**) crystals were obtained from the crude reaction mixture.

All complexes show rhenium in a slightly distorted octahedral geometry, with an average deviation from the ideal octahedral angles of 5.2−6.4°. For most geometrical parameters there is no significant difference between symmetrical and nonsymmetrical complexes. Among the exceptions is the N−Re−N angle, which in the symmetrical complexes (including $[ReO(salpd)]_2O$ (**3**)) adopts values of 94.2(3), 95.0(2), and 95.2(3)°, somewhat larger than the values encountered in the nonsymmetric complexes (91.6(2) and 93.4(2)°). The O−Re−O angle, formed by the two oxygen atoms of the salicylidene ligand, shows smaller values for the symmetrical complexes (83.3(3),

(17) NMR experiments in which the symmetrical methoxy complex was heated (60 °C) in 1,1,2,2-tetrachloroethane to induce the rearrangement resulted in precipitation of the μ-oxo complex.

82.1(2), and 81.9(3)°) than for the nonsymmetrical complexes (89.8(2) and 88.5(2)°). The N−Re−O angle of the five-membered chelate rings lies in the range 90.4(2)−91.4(2)°, except for the rings more or less perpendicular to the N−Re−N plane in the nonsymmetric complexes, which adopt values of 83.4(2) and 82.7(2)° for this angle.

Conclusion

It has been unambiguously proven that tetradentate Schiff base ligands of the sal_2en type coordinate to octahedral rhenium(V) to give symmetrical and nonsymmetrical complexes. Factors which influence the configuration of the complexes are the bridge length, the temperature of complex formation, and the nature of the second ligand.

For the first time two different configurational isomers of a rhenium−salen, the symmetrical and the nonsymmetrical ReO(salpd)OPr (**1c**) complex, have been synthesized via an indirect and direct synthetic route, respectively.

The indirect route enabled the configurationally controlled binding of a number of ligands including thiolates, acetate, and a phenolate, thus providing a useful pathway for the synthesis of a nearly unlimited number of new mixed-ligand complexes, which may have interesting properties.

By the linkage of a cholesteroxy ligand, it has been demonstrated that this method can be easily used for the linkage of biomolecules directly onto the rhenium core in a type of conjugate fashion rather than integrated.[18] This opens up the possibility of synthesizing isotope-labeled receptor-specific radiopharmaceuticals.

Finally, we have proven that a thermally induced rearrangement of the ligand around the rhenium center is possible, thus allowing to switch from symmetrical to non-symmetrical complexes. This configurational control provides us with a useful tool in the design of radiopharmaceuticals with a size and geometry, complementary to those of specific receptor sites.

Experimental Section

NMR spectra were recorded on a Bruker AC250 (^{1}H NMR 250 MHz) spectrometer in $CDCl_3$ unless otherwise stated. Residual solvent protons were used as an internal standard, and chemical shifts are given in ppm relative to tetramethylsilane (TMS). Fast atom bombardment (FAB) mass spectra were measured on a Finnigan MAT 90 spectrometer using *m*-nitrobenzyl alcohol (NBA) or *o*-nitrophenyloctyl ether (ONPOE) as a matrix. All solvents were purified by standard procedures. All other chemicals were analytically pure and were used without further purification. All reactions were carried out under an inert argon atmosphere. The presence of solvent in the analytical samples was confirmed by ^{1}H NMR spectroscopy. 2-Hydroxybenzaldehyde, ethylenediamine, 1,3-diaminopropane, and $ReO(PPh_3)_2Cl_3$ were used as received from Aldrich. The ligands *N*,*N*′-propane-1,3-diylbis(salicylideneamine), H_2salpd, and *N*,*N*′-butane-1,4-diylbis(salicylideneamine), H_2salbd, were prepared by mixing 2-hydroxybenzaldehyde and the appropriate diamine in a 2:1 stoichiometric ratio and recovering the Schiff base ligands by filtration as yellow solids. Melting points of all complexes could not be determined due to decomposition above 200 °C (Reichert melting point apparatus).

General Procedure for the Synthesis of the Complexes. To a refluxing solution of H_2salpd (**1**) (0.51 g, 1.80 mmol), or H_2salbd (**2**) (0.53 g, 1.80 mmol), in the appropriate alcohol (50 mL) were added $ReO(PPh_3)_2Cl_3$ (1.00 g, 1.20 mmol)[19] and Et_3N (1 mL, 7.20 mmol). The reaction mixture was refluxed for 4 h and then allowed to cool to room temperature. The resulting green precipitate was filtered off and washed with diethyl ether (50 mL). Yields are based on $ReO(PPh_3)_2Cl_3$. Concentration of the reaction mixture to increase the yields led to precipitation of PPh_3 and thus to impure products. No further attempts were made to increase the yields.

Symmetrical **Methoxy[*N*,*N*′-bis(salicylidene-1,3-diaminopropanato]oxorhenium(V) [ReO(salpd)OMe-sym, 1a].** The reaction was refluxed in methanol. Yield: 36%. ^{1}H NMR: δ 8.09 (s, 2 H, CH═N), 7.46 (t, 2 H, J = 6.8 Hz, ArH), 7.31 (d, 2 H, J = 7.9 Hz, ArH), 7.22 (d, 2 H, J = 7.9 Hz, ArH), 6.74 (t, 2 H, J = 6.8 Hz, ArH), 4.5−4.3 (m, 4 H, NCH_2), 3.24 (s, 3 H, OCH_3), 2.35−2.15 (m, 2 H, $CH_2CH_2CH_2$). ^{13}C NMR: δ 169.4 (CH═N), 58.2 (OCH_3). FAB-MS (*m*/*z* ^{187}Re, correct isotope pattern, NBA): 514.0 (M^+), 483.0 ($M - OMe)^+$. Anal. Calcd for $C_{18}H_{19}N_2O_4Re\cdot 0.5H_2O$: C, 41.37; H, 3.86; N, 5.36. Found: C, 41.67; H, 3.76; N, 5.40.

Symmetrical **Ethoxy[*N*,*N*′-bis(salicylidene)-1,3-diaminopropanato]oxorhenium(V) [ReO(salpd)OEt-sym, 1b].** The reaction was refluxed in ethanol. Yield: 35%. ^{1}H NMR: δ 8.05 (s, 2 H, CH═N), 7.46 (t, 2 H, J = 6.8 Hz, ArH), 7.30 (d, 2 H, J = 8.0 Hz, ArH), 7.21 (d, 2 H, J = 7.8 Hz, ArH), 6.73 (t, 2 H, J = 7.9 Hz, ArH), 4.5−4.3 (m, 4 H, NCH_2), 3.39 (q, 2 H, J = 7.0 Hz, OCH_2), 2.35−2.15 (m, 2 H, $CH_2CH_2CH_2$), 0.73 (t, 3 H, J = 6.9 Hz, CH_3). ^{13}C NMR: δ 169.5 (CH═N), 65.4 (OCH_2). FAB-MS (*m*/*z* ^{187}Re, correct isotope pattern, NBA): 528.6 (M^+), 483.6 ($M - OEt)^+$.[12]

Nonsymmetrical **Propoxy[*N*,*N*′-bis(salicylidene)-1,3-diaminopropanato]oxorhenium(V) [ReO(salpd)OPr-non-sym, 1c].** The reaction was refluxed in 1-propanol. Yield: 42%. ^{1}H NMR: δ 7.60 (s, 1 H, CH═N), 7.55 (t, 1 H, J = 7.8 Hz, ArH), 7.33 (d, 1 H, J = 8.2 Hz, ArH), 7.2−7.1 (m, 2 H, ArH), 7.13 (s, 1 H, CH═N), 7.0−6.85 (m, 3 H, ArH), 6.39 (d, 1 H, J = 8.2 Hz, ArH), 5.45−5.35, 4.85−4.75 (2 × m, 2 H, OCH_2), 5.0−4.85, 3.95−3.8, 3.65−3.3 (3 × m, 6 H, $CH_2CH_2CH_2$), 1.7−1.6 (m, 2 H, CH_3CH_2), 0.92 (t, 3 H, J = 7.4 Hz, CH_3). ^{13}C NMR: δ 171.0, 169.0 (CH═N), 70.6 (OCH_2). FAB-MS (*m*/*z* ^{187}Re, correct isotope pattern, ONPOE): 1084.7 (2 × $M)^+$, 483.5 ($M - OPr)^+$.[12]

Nonsymmetrical **Butoxy[*N*,*N*′-bis(salicylidene)-1,3-diaminopropanato]oxorhenium(V) [ReO(salpd)OBu-non-sym, 1d].** The reaction was refluxed in 1-butanol. Yield: 35%. ^{1}H NMR: δ 7.60 (s, 1 H, CH═N), 7.54 (t, 1 H, J = 7.8 Hz, ArH), 7.32 (d, 1 H, J = 8.2 Hz, ArH), 7.2−7.1 (m, 2 H, ArH), 7.12 (s, 1 H, CH═N), 7.0−6.8 (m, 3 H, ArH), 6.38 (d, 1 H, J = 8.2 Hz, ArH), 5.55−5.45, 4.85−4.75 (2 × m, 2 H, OCH_2), 5.0−4.85, 3.95−3.8, 3.65−3.3 (3 × m, 6 H, $CH_2CH_2CH_2$), 1.8−1.5 (m, 4 H, $CH_3CH_2CH_2$), 0.91 (t, 3 H, J = 7.3 Hz, CH_3). ^{13}C NMR: δ 171.0, 169.0 (CH═N), 70.0 (OCH_2). FAB-MS (*m*/*z* ^{187}Re, correct isotope pattern, ONPOE): 1112.8 (2 × $M)^+$, 483.5 ($M - OBu)^+$.[12]

***Nonsymmetrical iso*-Propoxy[*N*,*N*′-bis(salicylidene)-1,3-diaminopropanato]oxorhenium(V) [ReO(salpd)O*i*Pr-non-sym, 1e].** The reaction was refluxed in 2-propanol. Yield: 40%. ^{1}H NMR: δ 7.53 (s, 1 H, CH═N), 7.54 (t, 1 H, J = 7.8 Hz, ArH), 7.31 (d, 1 H, J = 8.2 Hz, ArH), 7.25−7.1 (m, 2 H, ArH), 7.10 (s, 1 H, CH═N), 7.05−6.85 (m, 3 H, ArH), 6.36 (d, 1 H, J = 8.2 Hz, ArH), 5.99 (qnt, 1 H, J = 4.9 Hz, OCH), 4.95−4.9, 3.95−3.7, 3.65−3.3 (3 × m, 6 H, $CH_2CH_2CH_2$), 1.33, 1.10 (2 × d, 2 × 1 H, J = 6.0 Hz, CH_3). ^{13}C NMR: δ 171.0, 168.6 (CH═N), ±77, coincides with solvent peak (OCH), 26.2, 24.9 (CH_3). FAB-MS (*m*/*z* ^{187}Re, correct isotope pattern, ONPOE): 1084.7 (2 × $M)^+$, 483.5 ($M - OPr)^+$.[12]

***Symmetrical tert*-Butoxy[*N*,*N*′-bis(salicylidene)-1,3-diaminopropanato]oxorhenium(V) [ReO(salpd)O*t*Bu-sym, 1f].** The reaction was refluxed in *tert*-butanol. Yield: 38%. ^{1}H NMR: δ 7.95 (s, 2 H, CH═N), 7.43 (t, 2 H, J = 6.8 Hz, ArH), 7.20 (d, 4 H, J = 8.2 Hz, ArH), 6.66 (t, 2 H, J = 7.9 Hz, ArH), 4.55−4.25 (m, 4 H, NCH_2), 2.35−2.1 (m, 2 H, $CH_2CH_2CH_2$), 0.75 (s, 9 H, *t*-Bu). ^{13}C NMR: δ 169.7 (CH═N), ±77, coincides with solvent peak (OC), 31.2 (CH_3). FAB-MS (*m*/*z* ^{187}Re, correct isotope pattern, ONPOE): 556.8 (M^+), 483.6 ($M - t$BuO)$^+$.[12]

Nonsymmetrical **Methoxy[*N*,*N*′-bis(salicylidene)-1,4-diaminobutanato]oxorhenium(V) [ReO(salbd)OMe-non-sym, 2a].** The reaction was refluxed in methanol. Yield: 40%. ^{1}H NMR: δ 7.99, 7.40 (2 × s, 2 × H, CH═N), 7.55 (t, 1 H, J = 6.8 Hz, ArH), 7.32 (d, 1 H, J = 7.7 Hz, ArH), 7.25 (d, 1 H, J = 7.6 Hz, ArH), 7.09 (d, 1 H, J = 7.6 Hz, ArH), 7.0−6.95 (m, 1 H, ArH), 6.85−6.75 (m, 2 H, ArH), 6.75

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(19) Substoichiometric amounts of $ReO(PPh_3)_2Cl_3$ were used to make sure that no $ReO(PPh_3)_2Cl_3$ would be left to contaminate the precipitating products.

(d, 1 H, J = 8.4 Hz, ArH), 4.8−4.6, 4.25−4.1, 3.9−3.8 (3 × m, 4 H, NCH_2, 3 × m, 4 H), 4.47 (s, 3 H, OCH_3), 2.4−1.95 (m, 4 H, $CH_2CH_2CH_2CH_2$). ^{13}C NMR: δ 171.1, 169.7 (CH═N), 68.0 (OCH_3). FAB-MS (*m/z* ^{187}Re, correct isotope pattern, NBA): 528.1 (M^+), 497.0 $(M - OMe)^+$. Anal. Calcd for $C_{19}H_{21}N_2O_4Re \cdot H_2O$: C, 42.53; H, 4.13; N, 5.22. Found: C, 42.23; H, 3.93; N, 5.13.

***Nonsymmetrical* Ethoxy[*N,N′*-bis(salicylidene)-1,4-diaminobutanato]oxorhenium(V) [ReO(salbd)OEt-non-sym, 2b].** The reaction was refluxed in ethanol. Yield: 45%. ^{1}H NMR: δ 7.98, 7.40 (2 × s, 2 H, CH═N), 7.54 (t, 1 H, J = 6.9 Hz, ArH), 7.3−7.2 (m, 2 H, ArH), 7.07 (d, 1 H, J = 7.6 Hz, ArH), 7.0−6.9 (m, 1 H, ArH), 6.85−6.75 (m, 2 H, ArH), 6.68 (d, 1 H, J = 8.2 Hz, ArH), 4.87 (q, 2 H, J = 7.0 Hz, OCH_2), 4.8−4.6, 4.25−4.1, 3.9−3.85 (3 × m, 4 H, NCH_2), 2.35−1.9 (m, 4 H, $CH_2CH_2CH_2CH_2$), 0.97 (t, 3 H, J = 7.0 Hz, CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.8, 169.7 (CH═N), 72.9 (OCH_2). FAB-MS (*m/z* ^{187}Re, correct isotope pattern, NBA): 542.9 (M^+), 497.0 $(M - OEt)^+$. Anal. Calcd for $C_{20}H_{23}N_2O_4Re$: C, 44.35; H, 4.28; N, 5.17. Found: C, 44.49; H, 4.24; N, 5.22.

***Nonsymmetrical* Propoxy[*N,N′*-bis(salicylidene)-1,4-diaminobutanato]oxorhenium(V) [ReO(salbd)OPr-non-sym, 2c].** The reaction was refluxed in 1-propanol. Yield: 41%. ^{1}H NMR: δ 7.98, 7.40 (2 × s, 2 H, CH═N), 7.54 (t, 1 H, J = 6.9 Hz, ArH), 7.35−7.25 (m, 2 H, ArH), 7.07 (d, 1 H, J = 7.6 Hz, ArH), 7.0−6.9 (m, 1 H, ArH), 6.85−6.75 (m, 2 H, ArH), 6.69 (d, 1 H, J = 8.2 Hz, ArH), 4.79 (t, 2 H, J = 6.6 Hz, OCH_2), 4.75−4.6, 4.3−4.05, 3.95−3.80 (3 × m, 4 H, NCH_2), 2.35−1.9 (m, 4 H, $CH_2CH_2CH_2CH_2$), 1.5−1.3 (m, 2H, CH_2CH_3), 0.97 (t, 3 H, J = 7.0 Hz, CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.7, 169.7 (CH═N), 73.0 (OCH_2). FAB-MS (*m/z* ^{187}Re, correct isotope pattern, NBA): 554.6 (M^+), 497.0 $(M - OPr)^+$.[12]

***Nonsymmetrical* Isopropoxy[*N,N′*-bis(salicylidene)-1,4-diaminobutanato]oxorhenium(V) [ReO(salbd)O*i*Pr-non-sym, 2d].** The reaction was refluxed in 2-propanol. Yield: 35%.^{1}H NMR: δ 7.95, 7.41 (2 × s, 2 H, CH═N), 7.52 (t, 1 H, J = 6.9 Hz, ArH), 7.23 (d, 1 H, J = 6.0 Hz, ArH), 7.06 (d, 1 H, J = 7.6 Hz, ArH), 6.95 (t, 1 H, J = 8.5 Hz, ArH), 6.85−6.75 (m, 2 H, ArH), 6.68 (d, 1 H, J = 8.2 Hz, ArH), 5.60 (septet, 1 H, J = 6.2 Hz, OCH), 4.75−4.7, 4.2−4.05, 3.95−3.85 (3 × m, 4 H, NCH_2), 2.4−1.85 (m, 4 H, $CH_2CH_2CH_2CH_2$), 1.24, 0.66 (d, 2 × 3 H, J = 6.2 Hz, CH_3). ^{13}C NMR: δ 170.6, 169.7 (CH═N), 78.1 (OCH). FAB-MS (*m/z* ^{187}Re, correct isotope pattern, NBA): 556.6 (M^+), 497.4 $(M - OiPr)^+$. Anal. Calcd for $C_{21}H_{25}N_2O_4Re$: C, 45.39; H, 4.54; N, 5.04. Found: C, 45.64; H, 4.64; N, 4.81.

***Nonsymmetrical* Chloro[*N,N′*-bis(salicylidene)-1,4-diaminobutanato]oxorhenium(V) [ReO(salbd)Cl-non-sym, 2e].** The reaction was refluxed in *tert*-butanol. Yield: 42%. ^{1}H NMR: δ 8.05, 7.65 (2 × s, 2 H, CH═N), 7.60 (t, 1 H, J = 6.9 Hz, ArH), 7.42 (d, 1 H, J = 8.3 Hz, ArH), 7.3−7.2 (m, 3 H, ArH), 7.1−7.0 (m, 2 H, ArH), 6.86 (d, 1 H, J = 7.2 Hz, ArH), 4.75−4.55, 4.3−4.2, 3.8−3.65 (3 × m, 4 H, NCH_2), 2.40−1.85 (m, 4 H, $CH_2CH_2CH_2CH_2$). FAB-MS (*m/z* ^{187}Re, correct isotope pattern, NBA): 531.9 (M^+), 496.9 $(M - Cl)^+$.[12]

General Procedure for Ligand Exchange. To a solution of ReO(salpd)OMe (**1a**) (0.50 g, 0.97 mmol) in refluxing CH_2Cl_2 (50 mL) was added a 10- to 15-fold excess of ligand. The mixture was refluxed for 12 h during which the methanol was trapped with 4 Å molecular sieves. The reaction mixture was allowed to cool to room temperature and was washed with 1 N NaOH (2 × 50 mL) and brine (50 mL) and dried ($MgSO_4$). The solvent was removed in vacuo to give the pure, green product in essentially quantitative yield.

***Symmetrical* Propoxy[*N,N′*-bis(salicylidene)-1,3-diaminopropanato]oxorhenium(V) [ReO(salpd)OPr-sym, 1c].** ^{1}H NMR: δ 7.99 (s, 2 H, CH═N), 7.39 (t, 2 H, J = 6.9 Hz, ArH), 7.23 (d, 2 H, J = 8.6 Hz, ArH), 7.14 (d, 2 H, J = 7.8 Hz, ArH), 6.66 (t, 2 H, J = 7.1 Hz, ArH), 4.45−4.25 (m, 4 H, NCH_2), 3.19 (t, 2 H, J = 6.7 Hz, OCH_2), 2.3−2.05 (m, 2 H, $CH_2CH_2CH_2$), 1.03 (sextet, 2 H, J = 7.2 Hz, CH_2CH_3) 0.37 (t, 3 H, J = 7.4 Hz, CH_3). ^{13}C NMR: 169.3 (CH═N), 71.9 (OCH_2). FAB-MS (*m/z* ^{187}Re, correct isotope pattern, ONPOE): 542.5 $(M)^+$, 483.5 $(M - OPr)^+$.[12]

***Symmetrical* (*p*-Methoxyphenoxy)[*N,N′*-bis(salicylidene)-1,3-diaminopropanato]oxorhenium(V) [ReO(salpd)O-Ph-OMe-sym, 1g].** ^{1}H NMR: δ 8.15 (s, 2 H, CH═N), 7.55 (t, 2 H, J = 6.8 Hz, ArH), 7.41 (d, 2 H, J = 8.3 Hz, ArH), 7.35 (d, 2 H, J = 6.2 Hz, ArH), 6.85 (t, 2 H, J = 6.8 Hz, ArH), 6.49, 5.93 (2 × d, 2 × 2 H, J = 9.0 Hz, Ar*H*−OMe), 4.4−4.2 (m, 4 H, NCH_2), 3.63 (s, 3 H, OCH_3), 2.10−1.95, 1.75−1.55 (2 × m, 2 × 1 H, $CH_2CH_2CH_2$). ^{13}C NMR: δ 170.2 (CH═N). FAB-MS (*m/z* ^{187}Re, correct isotope pattern, NBA): 606.0 (M^+), 482.9 $(M - O-Ph-OMe)^+$. Anal. Calcd for $C_{24}H_{23}N_2O_5Re$: C, 47.60; H, 3.83; N, 4.63. Found: C, 47.84; H, 3.88; N, 4.63.[12]

***Symmetrical* Acetoxy[*N,N′*-bis(salicylidene)-1,3-diaminopropanato]oxorhenium(V) [ReO(salpd)OAc-sym, 1h].** ^{1}H NMR: δ 8.00 (s, 2 H, CH═N), 7.48 (t, 2 H, J = 6.8 Hz, ArH), 7.33 (d, 2 H, J = 8.4 Hz, ArH), 7.23 (d, 2 H, J = 5.8 Hz, ArH), 6.78 (t, 2 H, J = 5.9 Hz, ArH), 4.8−4.75, 4.25−4.15 (2 × m, 2 × 2 H, NCH_2), 2.75−2.6, 2.35−2.2 (2 × m, 2 × 1 H, $CH_2CH_2CH_2$), 1.31 (s, 1 H, CH_3). ^{13}C NMR: δ 175.2 (C═O), 173.0, 170.9 (CH═N). FAB-MS (*m/z* ^{187}Re, correct isotope pattern, ONPOE): 542.0 (M^+), 482.9 $(M - OAc)^+$. Anal. Calcd for $C_{19}H_{19}N_2O_5Re$: C, 42.14; H, 3.54; N, 5.17. Found: C, 42.04; H, 3.57; N, 5.16.[12]

***Nonsymmetrical* (Ethylthio)[*N,N′*-bis(salicylidene)-1,3-diaminopropanato]oxorhenium(V) [ReO(salpd)SEt-non-sym, 1i].** ^{1}H NMR: δ 8.06, 7.80 (2 × s, 2 × 1 H, CH═N), 7.54 (t, 1 H, J = 8.6 Hz, ArH), 7.34 (d, 1 H, J = 8.3 Hz, ArH), 7.25−7.15 (m, 2 H, ArH), 7.06 (t, 1 H, J = 6.9 Hz, ArH), 6.85−6.8 (m, 2 H, ArH), 6.54 (d, 1 H, J = 8.4 Hz, ArH), 4.5−4.45, 4.0−3.95 (2 × m, 4 H, NCH_2), 3.75−3.5 (m, 2 H, SCH_2), 2.65−2.45, 2.35−2.15 (2 × m, 2 × 1 H, CH_2CH_2-CH_2), 1.33 (t, 3 H, J = 7.3 Hz, CH_3). ^{13}C NMR: δ 169.5, 167.3 (CH═N), 59.3 (SCH_2). FAB-MS (*m/z* ^{187}Re, correct isotope pattern, ONPOE): 544.8 $(M)^+$, 483.6 $(M - SEt)^+$. Anal. Calcd for $C_{19}H_{21}N_2O_3SRe$: C, 41.98; H, 3.89; N, 5.15; S, 5.90. Found: C, 41.88; H, 3.72; N, 5.09; S, 5.97.

***Nonsymmetrical* (Propylthio)[*N,N′*-bis(salicylidene)-1,3-diaminopropanato]oxorhenium(V) [ReO(salpd)SPr-non-sym, 1j].** ^{1}H NMR: δ 8.00, 7.74 (2 × s, 2 × 1 H, CH═N), 7.51 (t, 1 H, J = 7.0 Hz, ArH), 7.28 (d, 1 H, J = 8.4 Hz, ArH), 7.14 (d, 1 H, J = 7.8 Hz, ArH), 6.99 (t, 1 H, J = 7.0 Hz, ArH), 6.8−6.7 (m, 2 H, ArH), 6.48 (d, 1 H, J = 8.3 Hz, ArH), 4.45−4.4, 3.95−3.9 (2 × m, 2 × 1H, NCH_2), 3.65−3.4 (m, 2 H, SCH_2), 2.55−2.48, 2.25−2.1 (2 × m, 2 × 1 H, $CH_2CH_2CH_2$), 1.8−1.4 (m, 2 H, SCH_2CH_2), 0.87 (t, 3 H, J = 7.3 Hz, CH_3). ^{13}C NMR: δ 169.5, 167.3 (CH═N), 59.3 (SCH_2). FAB-MS (*m/z* ^{187}Re, correct isotope pattern, ONPOE): 559.8 (M^+), 483.5 $(M - SPr)^+$.[12]

***Symmetrical* Cholesteroxy[*N,N′*-bis(salicylidene)-1,3-diaminopropanato]oxorhenium(V) [ReO(salpd)OChol-sym, 1k].** ^{1}H NMR: δ 8.03, 8.00 (2 × s, 2 × 1 H, CH═N), 7.44 (t, 2 H, J = 6.7 Hz, ArH), 7.30 (d, 2 H, J = 5.8 Hz, ArH), 7.21 (d, 2 H, J = 8.3 Hz, ArH), 6.70 (t, 2 H, J = 5.9 Hz, ArH), 5.05−4.85 (m, 1 H, C═C*H*CH_2), 4.55−4.25 (m, 4 H, NCH_2), 3.2−3.05 (m, 1 H, OCH), 2.4−1.5 (m, 45 H, $CH_2CH_2CH_2$ + cholesterol signals). ^{13}C NMR: δ 169.6, 169.5 (CH═N). FAB-MS (*m/z* ^{187}Re, correct isotope pattern, NBA): 868.8 (M^+), 483.6 $(M - OChol)^+$.[12]

Crystal Structure Determinations of ReO(salbd)OPr (2c), [ReO(salpd)]$_2$O (3), and ReO(salpd)OPhOMe (1g). Crystals suitable for X-ray structure determination were glued to the top of a Lindemann glass capillary and transferred into the cold nitrogen stream on an Enraf-Nonius CAD4-T diffractometer on a rotating anode. Accurate unit-cell parameters and an orientation matrix were determined by least-squares fitting of the setting angles of a set of well-centered reflections (SET4). The unit-cell parameters were checked for the presence of a higher lattice symmetry.[20] Crystal data and details on data collection are collected in Table 3. Data were collected at 150 K in the ω scan mode using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å).

Data were corrected for *Lp* effects and for the linear decay of three periodically measured reference reflections during X-ray exposure time. The structures were solved by automated Patterson methods and subsequent difference Fourier techniques (SHELXS86).[21] Refinement on F^2 was carried out using full-matrix least-squares techniques (SHELXL-97);[22] no observance criterium was applied during refinement. For all

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Table 3. Crystallographic Data for ReO(salbd)OPr (**2c**), $[ReO(salpd)]_2O$ (**3**), and ReO(salpd)O-Ph-OMe (**1g**)

complex	ReO(salbd)OPr (**2c**)	$[ReO(salpd)]_2O$ (**3**)	ReO(salpd)O-Ph-OMe (**1g**)
formula	$C_{21}H_{25}N_2O_4Re{\cdot}CHCl_3$	$C_{34}H_{32}N_4O_7Re_2$	$C_{24}H_{23}N_2O_5Re$
mol weight	675.02	981.06	605.66
space group	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$P2_12_12_1$ (No. 19)
cryst system	triclinic	monoclinic	orthorhombic
Z	2	4	4
a, Å	10.0344(16)	14.860(2)	10.6222(15)
b, Å	10.647(2)	12.545(2)	12.442(3)
c, Å	11.481(2)	16.5111(17)	16.354(3)
α, deg	86.551(15)		
β, deg	86.998(14)	95.030(10)	
γ, deg	80.112(15)		
V, Å^3	1205.1(4)	3066.1(7)	2161.4(7)
D_{calcd}, g cm^{-3}	1.860	2.125	1.861
μ_{calcd}, cm^{-1} (MoKα)	54.1	79.5	56.6
R^a	0.0460 [4688; $I > 2\sigma(I)$]	0.0439 [5155; $I > 2\sigma(I)$]	0.0371 [3352; $I > 2\sigma(I)$]
w$R2^b$	0.1079	0.0886	0.0746
GoF	1.043	1.015	1.041

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

compounds refinement converged with a $\Delta/\sigma_{max} = 0.001$ and $\Delta/\sigma_{av} = 0.000$. Hydrogen atoms were included in the refinement on calculated positions riding on their carrier atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were included in the refinement with a fixed isotropic atomic displacement parameter related to the value of the equivalent isotropic atomic displacement parameter of their carrier atoms by a factor of 1.5 for the methyl hydrogen atoms and 1.2 for the other hydrogen atoms.

For ReO(salbd)OPr (**2c**) 5937 reflections were measured ($1.8° < \theta < 27.5°$, $-6 < h < 13$, $-13 < k < 13$, $-14 < l < 14$, $\Delta\omega = 0.50 + 0.35 \tan\theta°$), 5534 of which were unique ($R_{int} = 0.0715$) using a crystal of approximate dimensions of $0.05 \times 0.05 \times 0.2$ mm. No absorption correction was applied; 290 parameters were refined, and the final residual density was in the range $-2.59 < \Delta\rho < 1.78$ e Å^3 (near Re).

For $[ReO(salpd)]_2O$ (**3**) 10 246 reflections were measured ($1.2° < \theta < 27.5°$, $-19 < h < 19$, $-16 < k < 0$, $-21 < l < 14$, $\Delta\omega = 0.63 + 0.35 \tan\theta°$), 7016 of which were unique ($R_{int} = 0.0738$) using a crystal of approximate dimensions of $0.10 \times 0.15 \times 0.15$ mm. An empirical absorption correction was applied, based on ψ-scans (as implemented in PLATON,[20] transmission range 0.697−0.958); 427 parameters were refined, and the final residual density was in the range $-2.05 < \Delta\rho < 1.18$ e Å^3 (near Re).

For ReO(salpd)OPhOMe (**1g**) 7898 reflections were measured ($1.3° < \theta < 25.7°$, $-13 < h < 10$, $-16 < k < 12$, $-21 < l < 15$, $\Delta\omega = 0.82 + 0.35 \tan\theta°$), 3824 of which were unique ($R_{int} = 0.0588$) using a crystal of approximate dimensions of $0.10 \times 0.10 \times 0.30$ mm. An analytical absorption correction was applied (as implemented in PLATON,[20] transmission range 0.679−0.978); 290 parameters were refined, and the final residual density was in the range $-1.01 < \Delta\rho < 1.09$ e Å^3 (near Re). The Flack x parameter[23] derived during the final structure-factor calculation amounts to −0.013(15), indicating a correctly assigned absolute structure. Refinement of a racemic twin model gave a twin ratio of 1:0.

Neutral atom scattering factors and anomalous dispersion corrections were taken from ref 24. Geometrical calculations and illustrations were performed with PLATON.[20] All calculations were performed on a DEC Alpha station.

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Supporting Information Available: X-ray crystallographic files of ReO(salbd)OPr (**2c**), ReO(salbd)O*i*Pr (**2d**), $[ReO(salpd)]_2O$ (**3**), and ReO(salpd)O-Ph-OMe (**1g**), in CIF format, and an atomic displacement ellipsoid plot of **2d** are available on the Internet only. Access information is given on any current masthead page.

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