1988 *Inorg. Chem.* **1996,** *35,* 1988−1991

Multiple Bonds between Main Group Elements and Transition Metals. 153.[1] Rhenium(V) Oxo Complexes with Tetradentate Schiff Bases: Structural Considerations

Wolfgang A. Herrmann,* Monika U. Rauch, and Georg R. J. Artus

Anorganisch-chemisches Institut der Technischen Universität München, Lichtenbergstrasse 4,
D-85747 Garching, Germany

Received July 7, 1995[⊗]

The reactions of [NBu$_4$][ReOCl$_4$] with potentially tetradentate bis(salicylidene)amine ligands (sal$_2$en = H$_2$L) have been investigated. The bimetallic rhenium(V) complex [NBu$_4$]$_2$[Re$_2$O$_2$Cl$_6$(L)] (**2a**) is formed if the ligand precursor H$_2$L contains *two* CH$_2$ units bridging the imino groups of the sal$_2$en fragments, while monomeric octahedral rhenium(V) compounds [ReOCl(L)] (**2b**−**d**) are formed if *three* carbon atoms form the bridge. In contrast to similar technetium compounds where a symmetrical equatorial arrangement is observed, the rhenium complex exhibits an asymmetric nonplanar coordination of the ligand. The crystal structures of mono- and bimetallic derivatives have been determined. Crystal data are as follows: **2a**, monoclinic, space group $P2_1/c$, $a = 23.003(3)$ Å, $b = 13.385(1)$ Å, $c = 24.344(4)$ Å, $\beta = 93.88(7)°$, $R = 0.045$ for 7974 reflections; **2b**, monoclinic, space group $P2_1/n$, $a = 12.094(2)$ Å, $b = 15.410(2)$ Å, $c = 14.857(3)$ Å, $\beta = 108.49(2)°$, $R = 0.034$ for 3415 reflections; **2c**, monoclinic, space group $P2_1/n$, $a = 10.748(1)$ Å, $b = 16.695(2)$ Å, $c = 10.893(2)$ Å, $\beta = 105.61(1)°$, $R = 0.028$ for 2736 reflections.

Introduction

Rhenium and technetium complexes with Schiff base ligands derived from salicylaldehyde and mono- or diamines have received attention for various reasons.[2−15] Particular interest in these compounds stems from the extensive use of ^{99m}Tc in nuclear medicine and the potential of ^{186}Re to serve as a nuclide in radiotherapy.[16] On the other hand chiral bis(salicylidene)amine complexes of manganese(III) are efficient catalysts in the enantioselective oxidation of olefins.[17] We became thus challenged by the rhenium chemistry of such ligands, especially since high-valent organorhenium oxides catalyze olefin oxidation.[18] In this paper we present structural and first catalytical work related to tetradentate sal$_2$en ligands attached to pentavalent rhenium centers.

Experimental Section

All reactions were performed with standard Schlenck techniques in an oxygen-free nitrogen atmosphere. Solvents were dried with standard methods and distilled under N$_2$. Infrared spectra were recorded on a Perkin-Elmer 1600 series FTIR spectrometer, the ^{1}H and ^{13}C spectra at 400 and 100.54 MHz, respectively, on a FT Jeol GX 400 instrument. Elemental analyses were performed in the Microanalytical Laboratory of our institute (M. Barth). Mass spectra were obtained with Finnigan MAT 311A and MAT 90 spectrometers. Tetra-*n*-butylammonium tetrachlorooxorhenate(V) was prepared as reported in ref 19. 2-Hydroxybenzaldehyde, 3,5-dichloro-2-hydroxybenzaldehyde, 2,2-dimethylpropyldiamine, and ethylenediamine were used as received from Aldrich. 3,5-Di-*tert*-butyl-2-hydroxybenzaldehyde was prepared as reported in the literature.[20] Ligands **1a**−**d** were prepared by mixing the substituted benzaldehydes and amines in a 2:1 stoichiometric ratio and recovering the Schiff base ligands by filtration as yellow solids.

[⊗] Abstract published in *Advance ACS Abstracts,* March 1, 1996.

(1) Preceding paper of this series. Part 152: Laurenczy, G.; Lukács, F.; Roulet, R.; Herrmann, W. A.; Fischer, R. W. *Organometallics* **1996**, *15*, 848.

(2) Bombieri, G.; Mazzi, U.; Gilli, G.; Hernandez-Cano, F. *J. Organomet. Chem.* **1978**, *159*, 53.

(3) Middleton, A. R.; Masters, A. F.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1979**, 542.

(4) Mazzi, U.; Roncari, E.; Rossi, R.; Bertolasi, V.; Traverso, O.; Magon, L. *Trans. Met. Chem.* **1980**, *5*, 289.

(5) Duatti, A.; Rossi, R.; Magon, L.; Mazzi, U. *Trans. Met. Chem.* **1983**, *8*, 170.

(6) Bandoli, G.; Nicolini, M.; Mazzi, U.; Refosco, F. *J. Chem. Soc., Dalton Trans.* **1984**, 2505.

(7) Jurisson, S.; Lindoy, L. F.; Dancey, K. P.; McPartlin, M.; Tasker, P. A.; Uppal, D. K.; Deutsch, E. *Inorg. Chem.* **1994**, *23*, 227.

(8) Bandoli, G.; Mazzi, U.; Wilcox, B. E.; Jurisson, S.; Deutsch, E. *Inorg. Chim. Acta* **1984**, *95*, 217.

(9) Marchi, A.; Duatti, A.; Rossi, R.; Magon, L.; Mazzi, U.; Pasquetto, A. *Inorg. Chim. Acta* **1984**, *81*, 15.

(10) Mazzi, U.; Refosco, F.; Bandoli, G.; Nicolini, M. *Trans. Met. Chem.* **1985**, *10*, 121.

(11) Mazzi, U.; Refosco, F.; Tisato, F.; Bandoli, G.; Nicolini, M. *J. Chem. Soc., Dalton Trans.* **1986**, 1623.

(12) Tisato, F.; Refosco, F.; Mazzi, U.; Bandoli, G.; Dolmella, A. *Inorg. Chim. Acta* **1989**, *164*, 127.

(13) Refosco, F.; Tisato, F.; Mazzi, U.; Bandoli, G.; Nicolini, M. *J. Chem. Soc., Dalton Trans.* **1988**, 611.

(14) Tisato, F.; Refosco, F.; Moresco, A.; Bandoli, G.; Mazzi, U.; Nicolini, M. *J. Chem. Soc., Dalton Trans.* **1990**, 2225.

(15) Tisato, F.; Refosco, F.; Mazzi, U.; Bandoli, G.; Nicolini, M. *Inorg. Chim. Acta* **1991**, *189*, 97.

(16) (a) Deutsch, E.; Libson, K. *Comments Inorg. Chem.* **1984**, *3*, 83. (b) Clarke, M. J.; Podbielsky, L. *Coord. Chem. Rev.* **1987**, *78*, 253. (c) Griffiths, G. L.; Goldenberg, D. M.; Jones, A.; Hansen, H. *J. Bioconjugate Chem.* **1992**, *3*, 91. (d) Jurisson, S.; Berning, D.; Jia, W.; Ma, D. *Chem. Rev.* **1993**, 1137.

(17) (a) Zhang, W.; Loebach, J. L.; Wilson, S. R.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1990**, *112*, 2801. (b) Jacobsen, E. N.; Zhang, W.; Muci, A. R.; Ecker, J. R.; Deng, L. J. *J. Am. Chem. Soc.* **1991**, *113*, 7063. (c) Zhang, W.; Jacobsen, E. N. *J. Org. Chem.* **1991**, *56*, 2296. (d) Jacobsen, E. N. In *Catalytic Asymmetric Synthesis*, Ojima, I., Ed.; VCH: New York, 1993. (e) Chang, S.; Heid, R. M.; Jacobsen, E. N. *Tetrahedron Lett.* **1994**, *35*, 669. (f) Palucki, M.; Pospisil, P. J.; Zhang, W.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1994**, *116*, 9333. (g) Larrow, J. F.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1994**, *116*, 12129.

(18) (a) Herrmann, W. A.; Fischer, R. W.; Rauch, M. U.; Scherer, W. *J. Mol. Catal.* **1994**, *86*, 243. (b) Herrmann, W. A.; Fischer, R. W.; Marz, D. W. *Angew. Chem.* **1991**, *103*, 1706; *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1638. (c) Herrmann, W. A.; Fischer, R. W.; Scherer, W.; Rauch, M. U. *Angew. Chem.* **1993**, *105*, 1209; *Angew. Chem., Int. Ed. Engl.* **1993**, *30*, 1157.

(19) Alberto, R.; Schibli, R.; Egli, A.; Schubiger, P. A.; Herrmann, W. A.; Artus, G.; Abram, U.; Kaden, T. A. *J. Organomet. Chem.* **1995**, *492*, 217.

(20) Casiraghi, G.; Casnati, G.; Puglia, G.; Sartori, G.; Terenghi, G. *J. Chem. Soc., Perkin Trans.* **1980**, 1862.

(21) (a) IPDS Operating system 1994. (b) Frenz, B. A. *SDP*; Enraf-Nonius: Delft, The Netherlands, **1988**. (c) Sheldrick, G. M. *SHELXS-86*; Universität Göttingen, FRG, **1986**. (d) Watkin, D. J.; Betteridge, P. W.; Carruthers, J. R. *CRYSTALS User Manual*; Oxford, England, 1986. (e) Spek, A. L. PLATON. *Acta Crystallogr.* **1990**, *A46*, C34.

0020-1669/96/1335-1988$12.00/0

Table 1. Structure Determination Summary

	2a	2b	2c
formula	$C_{64}H_{118}Cl_6N_4O_4Re_2$	$C_{19}H_{16}Cl_5N_2O_3Re \cdot CH_2Cl_2$	$C_{19}H_{20}ClN_2O_3Re$
M_r	1592.79	683.82 + 84.93	546.04
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)
a (Å)	23.003(3)	12.094(2)	10.748(1)
b (Å)	13.385(1)	15.410(2)	16.695(2)
c (Å)	24.344(4)	14.857(3)	10.893(2)
β (deg)	93.88(7)	108.49(2)	105.61(1)
V (Å^3)	7478	2626	1883
D_{calc} (g cm^{-3})	1.41	1.94	1.93
Z	4	4	4
F(000)	3256	1480	1056
μ (cm^{-1})	34.9	53.7	66.2
Mo Kα (Å)	0.710 73	0.710 73	0.710 73
diffractometer	CAD4 (Enraf Nonius)	IPDS (STOE)	IPDS (STOE)
Θ range deg	$1 < \Theta < 25$	$3.55 < \Theta < 24.2$	$3.55 < \Theta < 24.2$
temp (°C)	-50 ± 3	26 ± 2	26 ± 2
abs corr	ψ-Scans	ref 21a	ref 21a
data measd	14128	17379	21626
unique data	10942	4114	2778
reflcns used	7974	3415	2736
$I/\sigma(I)$	>3.0	>1.0	>0.0
no. of params	704	298	315
weighting scheme	ref 22	$w = 1$	ref 22
residual electron density (e Å^{-3})	+1.8, −1.0	+1.1, −0.9	+1.3, −1.8
R^a	0.045	0.034	0.028
$R_w{}^b$	0.045	0.038	0.030

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

(1) Bis(tetra-*n*-butylammonium) Hexachloro(*μ*-(*N,N′*-ethylenebis-(3,5-di-*tert*-butylsalicylideneaminato))dioxodirhenate(V) (2a). A 493 mg (1 mmol) amount of *N,N′*-bis(3,5-di-*tert*-butyl)salicylidene)ethylenediamine (**1a**) was added to a solution of 293 mg (0.5 mmol) of $[NBu_4][ReOCl_4]$ in 20 mL of dry ethanol. The reaction mixture was refluxed for 3 h and then stirred for 16 h at room temperature. The green solution was slowly concentrated until yellow crystals of **1a**·2HCl precipitate formed. The filtrate was concentrated to a small volume and layered with Et_2O. Green crystals were collected and washed with pentane. Yield 60%. Anal. Calcd for $C_{64}H_{118}N_4O_4Re_2Cl_6$: C, 48.26; H, 7.47; N, 3.53; Re, 23.38. Found: C, 47.86; H, 7.55; N, 3.68; Re, 23.98. IR (KBr, cm^{-1}): ν(CH=N) 1606.9, ν(C−O) 1259.2, ν(Re=O) 963.0. ^{1}H NMR ($CDCl_3$, 400 MHz, RT, ppm): δ 0.95 ($N(CH_2)_3CH_3$, tr, $^3J = 7.3$ Hz, 24H), 0.99 ($C(CH_3)_3$, s, 18H), 1.31 ($C(CH_3)_3$, s, 18H), 1.41 ($N(CH_2)_2CH_2$, m, 16H), 1.66 ($N(CH_2)CH_2$, m, 16H), 3.24 (NCH_2, m, 16H), 4.64 (H8, s, 4H), 6.69 (H3, d, $^4J_{H3,H5}$ = 2.4 Hz, 2H), 7.0 (H5, d, 2H), 7.87 (H7, s, 2H).

(2) Chloro[1,3-(*N,N′*-bis-(3,5-dichlorosalicylidene)diamino)-2,2-dimethylpropyl]oxorhenium(V) (2b), Chloro[1,3-(*N,N′*-bis(salicylidene)diamino)-2,2-dimethylpropyl]oxorhenium(V) (2c), Chloro-[1-3-(*N,N′*-bis-(3,5-di-*tert*-butylsalicylidene)diamino)-2,2-dimethylpropyl]oxorhenium(V) (2d). The same procedure as above was followed using **1b**−**d**: 1.0 mmol of **1b**−**d** was added to a solution of 293 mg (0.5 mmol) of $[NBu_4][ReOCl_4]$ in 20 mL of dry ethanol. The reaction mixture was refluxed for 3 h. The resulting green precipate was collected after cooling by filtration and washed with pentane. Yield 65−85%.

2b. Anal. Calcd for $C_{19}H_{16}Cl_5N_2ReO_3$: C, 33.37; H, 2.36; N, 4.10; Cl, 25.92. Found: C, 33.32; H, 2.65; N, 4.09; Cl, 26.01. IR (KBr, cm^{-1}): ν(CH=N) 1614.5, 1597.2; ν(C−O) 1288.0, 1310.0, ν(Re=O) 952.3. ^{1}H NMR [(DMSO-d_6, 400 MHz, RT, ppm): δ 0.72 (CH_3, s, 3H), 1.22 (CH_3, s, 3H), 3.81 (H8a, d, $^2J_{H8a,H8b}$ = 13.2 Hz, 1H), 4.16 (H8′a, d, $^2J_{H8'a,H8'b}$ = 10.5 Hz, 1H), 4.28 (H8b, d, 1H) 4.81 (H8′b, d, 1H), 7.50 (H3′, d, $^4J_{H3',H5'}$ = 2.9 Hz, 1H), 7.60 (H5′, d, 1H), 7.62 (H5, d, $^4J_{H5,H3}$ = 2.9 Hz, 1H), 7.94 (H3, d, 1H), 7.86 (H7′, s, 1H), 8.10 (H7, s, 1H).

2c. Anal. Calcd for $C_{19}H_{20}ClN_2ReO_3$: C, 41.79; H, 3.69; N, 5.13; Cl, 6.49. Found: C, 41.66; H, 3.98; N, 4.93; Cl, 6.74. IR (KBr, cm^{-1}): ν(CH=N) 1616.1, 1604.0; ν(C−O) 1284.9; ν(Re=O) 956.7. ^{1}H NMR ($CDCl_3$, 400 MHz, RT, ppm): δ 0.92, 1.17 (H10, H10′, 2 × s, 2 × 3H), 3.87 (H8, dd, $^2J_{H8a,H8b}$ = 13.6 Hz, 2H), 4.14 (H8′a, d, $^2J_{H8'a,H8'b}$ = 11.1 Hz, 1H), 4.74 (H8′b, d, 1H), 6.85 (H5′, d, $^3J_{H5',H4'}$ = 8.1, 1H), 7.00 (H3, tr, $^3J_{H3,H4}$ = 7.2, 1H), 7.19 (H3′, d, $^3J_{H3',H4'}$ = 7.0 Hz, 1H), 7.26 (H5, H4′, m, 2H), 7.59 (H2, d, $^3J_{H2,H3}$ = 6.7 Hz, 1H), 7.62 (H2′, d, $^3J_{H2',H3'}$ = 7.6 Hz, 1H), 7.73 (H4, tr, $^3J_{H4,H5}$ = 7.1 Hz, 1H), 8.00 (H7′, s, 1H), 8.51 (H7, s, 1H). EI-MS (*m/z*, ^{187}Re, correct isotope pattern): 546.3 (M$^+$), 411.3 (M − Cl)$^+$.

2d. Anal. Calcd for $C_{35}H_{52}ClN_2ReO_3$: C, 54.56; H, 6.80; N, 3.64; Cl, 4.60. Found: C, 54.55; H, 6.99; N, 3.73; Cl, 4.66. IR (KBr, cm^{-1}): ν(CH=N) 1609.7; ν(C−O) 1276.4, 1250.3; ν(Re=O) 952.8. ^{1}H NMR ($CDCl_3$, 400 MHz, RT, ppm): δ 0.86, 1.08 (H10, H10′, 2 × s, 2 × 3H), 1.11 ($C(CH_3)_3$, s, 9H), 1.27 ($C(CH_3)_3$, s, 9H), 1.31 ($C(CH_3)_3$, s, 9H), 1.54 ($C(CH_3)_3$, s, 9H), 3.57 (H8′, dd, $^2J_{H8'a,H8'b}$ = 11.7 Hz, 2H), 4.36 (H8, dd, $^4J_{H8a,H8b}$ = 13.0 Hz, 2H), 6.99 (H5, d, $^4J_{H5,H3}$ = 2.4, 1H), 7.13 (H5′, d, $^4J_{H5',H3'}$ = 2.4 Hz, 1H), 7.19 (H3′, d, 1H), 7.65 (H3, d,

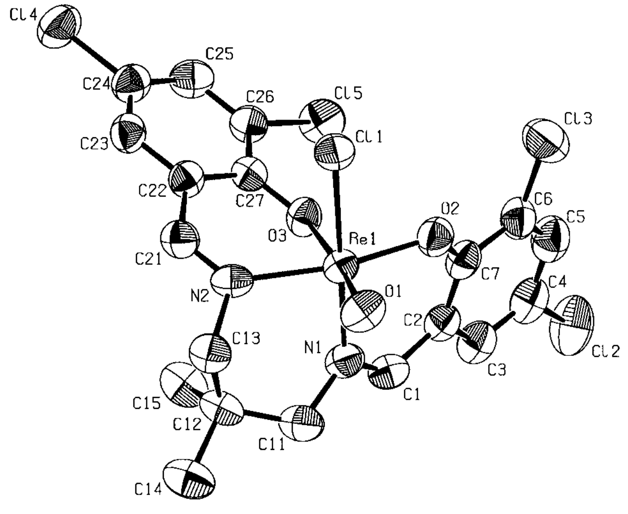


Figure 1. PLATON plot^{21e} of **2b**. Ellipsoids are at the 50% probability level; hydrogen atoms, omitted for clarity. Selected bond lengths (Å) and angles (deg): Re1−Cl1 = 2.393(2), Re1−O1 = 1.679(5), Re1−O2 = 1.976(5), Re1−O3 = 1.994(5), Re1−N1 = 2.077(7), Re1−N2 = 2.055(7), O1−Re1−Cl1 = 94.2(2), O2−Re1−Cl1 = 88.2(2), O2−Re1−O1 = 103.0(3), O3−Re1−Cl1 = 87.1(2), O3−Re1−O1 = 174.1(3), O3−Re1−O2 = 82.8(2), N1−Re1−Cl1 = 175.0(2), N1−Re1−O1 = 90.8(3), N1−Re1−O2 = 90.3(2), N1−Re1−O3 = 88.1(2), N2−Re1−Cl1 = 90.7(2), N2−Re1−O1 = 94.5(3), N2−Re1−O2 = 162.4(2), N2−Re1−O3 = 79.6(2), N2−Re1−N1 = 89.3(3).

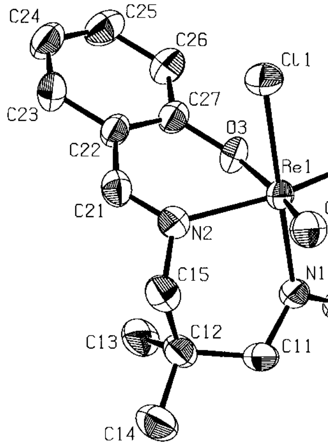


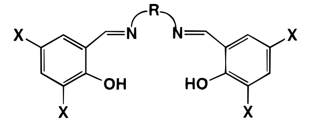
Figure 2. PLATON plot[21e] of **2c**. Ellipsoids are at the 50% probability level; hydrogen atoms, omitted for clarity. Selected bond lengths (Å) and angles (deg): Re1−Cl1 = 2.390(1), Re1−O1 = 1.680(3), Re1−O2 = 1.995(3), Re1−O3 = 1.981(3), Re1−N1 = 2.092(4), Re1−N2 = 2.096(3), O1−Re1−Cl1 = 92.7(1), O2−Re1−Cl1 = 87.60(9), O2−Re1−O1 = 103.5(2), O3−Re1−Cl1 = 85.72(9), O3−Re1−O1 = 172.5(1), O3−Re1−O2 = 83.7(1), N1−Re1−Cl1 = 177.3(1), N1−Re1−O1 = 89.8(1), N1−Re1−O2 = 90.8(1), N1−Re1−O3 = 91.9(1), N2−Re1−Cl1 = 91.35(9), N2−Re1−O1 = 91.9(1), N2−Re1−O2 = 164.6(1), N2−Re1−O3 = 80.9(1), N2−Re1−N1 = 89.6(1).

1H), 7.42 (H7′, s, 1H), 7.74 (H7, s, 1H). CI-MS (*m/z*, ^{187}Re, correct isotope pattern): 770.7 (M$^+$).

(3) X-ray Crystal Analyses. All carbon atoms of one of the cations in **2a** are disordered. The disorder could be resolved completely. All hydrogen atoms in **2a** and **2b** were calculated, the hydrogen atoms in **2c** were found by difference Fourier methods and refined with isotropic displacement parameters. All calculations were performed with the program systems listed in ref 21. Relevant crystallographic data and structure determination parameters are given in Table 1. For selected interatomic distances and bond angles, see Figures 1−3.

Results and Discussion

Rhenium(V) sal$_2$en complexes have been synthesized from the free ligands **1a−d** containing two- and three-carbon alkyl chains that bridge the imino groups. The reactions follow eq 1 when 2 equiv of the ligands H$_2$L are used.[15] One equivalent serves as a ligand; another equivalent, as a base to deprotonate the phenolic hydroxy functions and to remove the 2 equiv of HCl that are released in the substitution reaction. The use of triethylamine is known in the literature[3,4,15] and seems justified in the case of expensive ligands. The four possible configurations of *O,N,N,O*-tetradentate Schiff bases are seen in the structure types **A−D**.

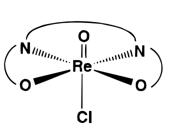


1a-d

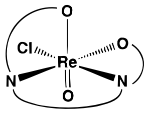
	a	b	c	d
X	^{t}Bu	Cl	H	^{t}Bu
R	-CH$_2$-CH$_2$-	-CH$_2$-C(CH$_3$)$_2$-CH$_2$-		

$$2\,[NBu_4][ReOCl_4] + 2\,\underset{\textbf{1a}}{H_2L} \xrightarrow{EtOH} \underset{\textbf{2a}}{[NBu_4]_2[Re_2O_2Cl_6(L)]} + H_2L\bullet 2HCl \quad (1a)$$

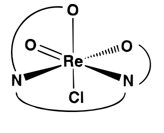
$$[NBu_4][ReOCl_4] + 2\,\underset{\textbf{1b-d}}{H_2L} \xrightarrow{EtOH} \underset{\textbf{2b-d}}{ReOCl(L)} + [NBu_4]Cl + H_2L\bullet 2HCl \quad (1b)$$



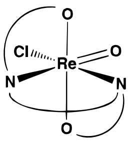
A



B + enant.

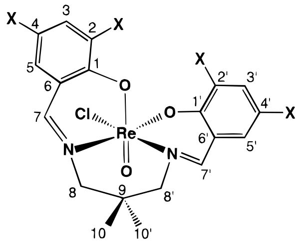


C + enant.



D + enant.

In the C_s symmetric complex **A** all metal-bonded functional groups of the ligand are located in the equatorial plane of the molecule, just like in the five-coordinate manganese(III) complexes [Mn(sal$_2$en)Cl].[23] This structure is known for six-coordinate technetium(V) complexes bearing a chlorine atom in the *trans* position to the Tc=O moiety[6,7] and has also been postulated for six-coordinate rhenium(V) complexes with ligands containing up to four carbon atoms bridging the imino groups.[3,9,12,15] However, these assignments are only based on spectroscopic evidence and appear rather weakly supported by the analogy to Tc(V) derivatives. No structural investigations, e.g. X-ray diffraction analyses, are known. Considering the strong *trans* influence of an oxo ligand, structures of type **A** seem unfavorable. In fact, in rhenium complexes resulting from type **1** ligands a chloro ligand coordinated *trans* to Re=O$_{oxo}$ has never been observed. Complexes of types **B−D** are thus more likely to occur. All three complexes are chiral as a result of the missing symmetry. X-ray structure analyses of compounds **2b** and **2c** confirm the structural type **B**.



2b-d

	b	c	d
X	Cl	H	^{t}Bu

The two halves of the sal$_2$en ligand are perpendicular to each other. One *N,O*-unit of **B** is located in the equatorial plane, with the phenolate oxygen atom being *trans* to the Re=O moiety resulting in a facial *N*,*O*$_{oxo}$,*N*-arrangement (Figures 1 and 2). This geometry is in contrast to earlier statements[3,9,12,15] and underlines the preferred binding of a relatively hard phenoxy donor ligand *trans* to the Re=O moiety. ^{1}H NMR data support the asymmetric arrangement of the sal$_2$en fragments (all protons in different chemical environments). The NMR spectra were assigned by means of ^{1}H,^{1}H-COSY experiments. The IR spectra exhibit two well-separated stretching bands [ν(CH=N) = 1615 and 1597 cm^{-1}, **2b**; ν(CH=N) = 1616 and 1604 cm^{-1}, **2c**]. The ν(Re=O) bands at 952 and 957 cm^{-1}, respectively, fall in the typical range of Schiff base Re(V) complexes.[4,10,12,15]

---

(22) Prince, E. *Mathematical Techniques in Crystallography*; Springer-Verlag: Berlin, 1982.

(23) (a) Davies, J. E.; Gatehouse, B. M.; Murray, K. S. *J. Chem. Soc., Dalton Trans.* **1973**, 2523. (b) Akhtar, F.; Drew, M. G. B. *Acta Crystallogr.* **1982**, *B38*, 612. (c) Srinivasan, K.; Michaud, P. *J. Am. Chem. Soc.* **1986**, *108*, 2309. (d) Pecoraro, V. L.; Butler, W. M. *Acta Crystallogr.* **1986**, *C42*, 1151. (e) Oki, A. R.; Hodgson, D. J. *Inorg. Chim. Acta* **1990**, *170*, 65. (f) Pritchard, R. G.; McAuliffe, C. A.; Parish, R. V.; Nabhan, A. A. J.; Ashmawy, F. M.; Garcia-Deibe, A.; Sousa, A.; Bermejo, M. R. *Acta Crystallogr.* **1991**, *C47*, 2453.

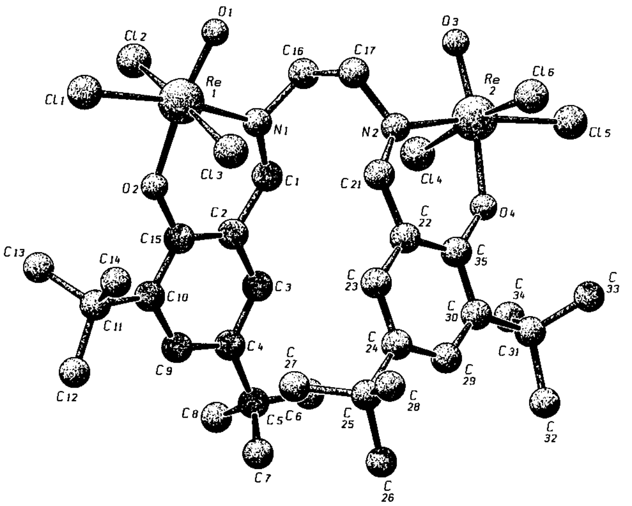


Figure 3. PLATON plot[21e] of **2a**. Ellipsoids are at the 50% probability level; hydrogen atoms, and cations omitted for clarity. Selected bond lengths (Å) and angles (deg): Re1−Cl1 = 2.375(2), Re1−Cl2 = 2.386(2), Re1−Cl3 = 2.428(2), Re1−O1 = 1.689(6), Re1−O2 = 1.956(5), Re1−N1 = 2.106(6), Re2−Cl4 = 2.405(2), Re2−Cl5 = 2.362(2), Re2−Cl6 = 2.388(2), Re2−O3 = 1.690(5), Re2−O4 = 1.947(5), Re2−N2 = 2.122(5), Cl2−Re1−Cl1 = 90.75(7), Cl3−Re1−Cl1 = 91.51(7), Cl3−Re1−Cl2 = 174.79(8), O1−Re1−Cl1 = 100.1(2), O1−Re1−Cl2 = 94.0(2), O1−Re1−Cl3 = 90.2(2), O2−Re1−Cl1 = 86.7(1), O2−Re1−Cl2 = 90.8(2), O2−Re1−Cl3 = 84.6(2), O2−Re1−O1 = 171.5(3), N1−Re1−Cl1 = 168.7(2), N1−Re1−Cl2 = 84.6(2), N1−Re1−Cl3 = 92.4(2), N1−Re1−O1 = 90.5(2), N1−Re1−O2 = 83.1(2), Cl5−Re2−Cl4 = 91.10(9), Cl6−Re2−Cl4 = 172.65(9), Cl6−Re2−Cl5 = 89.84(9), O3−Re2−Cl4 = 92.2(2), O3−Re2−Cl5 = 99.1(2), O3−Re2−Cl6 = 94.8(2), O4−Re2−Cl4 = 85.3(2), O4−Re2−Cl5 = 89.4(2), O4−Re2−Cl6 = 87.4(2), O4−Re2−O3 = 171.2(2), N2−Re2−Cl4 = 92.5(2), N2−Re2−Cl5 = 170.2(2), N2−Re2−Cl6 = 85.4(2), N2−Re2−O3 = 89.9(2), N2−Re2−O4 = 81.8(2).

Analogous spectra were obtained for **2d**. The ^1H NMR spectra show a doubled set of resonances due to the asymmetric coordination of the ligand. The $\nu(CH{=}N)$ stretching mode in the IR spectra is split into two vibrations centered at 1612 cm^{-1}, and the $\nu(Re{=}O)$ band occurs at 952 cm^{-1}.

The coordination of type **B** was suggested for ligands containing five or more atoms in the bridging chain[15] and was observed for rhenium(V) complexes with type **1** ligands, where R represents $-(CH_2)_2O(CH_2)_2O(CH_2)_2-$[24] and $-(CH_2)_2S(CH_2)_2-$.[25] **B** is also found in complexes with two independent and unbridged *N,O* bidentate Schiff base ligands derived from salicylaldehyde and monoamines.[26] Structures **C** and **D** have not yet been observed with this same type of ligand. In case of **C** this can be explained by the less favored coordination of an imino nitrogen donor *trans* to $Re{=}O_{oxo}$. Considering the 2-fold symmetry in the ligand resulting in complex **D** and assuming planar conformation at the imino nitrogen atoms, the bridge between the two imino functions had to adopt a serpentlike conformation. Even with a very long bridge, this type of coordination seems disadvantageous. The importance of the length of the bridging chain can be seen in the crystal structure of **2a** (Figure 3). One ligand was found to bridge two rhenium atoms that present a distorted octahedral coordination. Again both phenolate oxygen atoms are in *trans* positions to the Re═O moiety. The appearance of a single set of ^1H NMR resonances for both *N,O*-units proves their chemical identity, which is also supported by the IR data: only one stretching frequency is observed for the imino double bonds ($\nu(CH{=}N)$ = 1607 cm^{-1}, KBr). Similar findings are reported for a complex of composition $[(C_6H_5)_4As]_2[Re_2O_2Cl_6(sal_2en)]$ for which, however, no crystal structure is known.[9]

Table 2. Epoxidation of *cis*-Cyclooctene by 1.0 mol % of Catalysts **2b−d**

complex	reaction time (h)	cyclooctene conversion (%)	cyclooctene oxide yield (%)	side products
2b	10	75	66	2-*tert*-butoxycyclooctanol
2c	10	70	60	2-*tert*-butoxycyclooctanol
2d	10	68	59	2-*tert*-butoxycyclooctanol

By forming a bimetallic complex, this system avoids the equatorial arrangement of the ligand with a chlorine atom *trans* to an oxo ligand (type **A**). The preferred coordination of type **B** as found in the complexes **2b,c** is then impossible for steric reasons. Because of the orthogonality of the two aromatic systems and the planarity of the imino nitrogen atoms, the bridging of the two *N,O*-units with less than three atoms would result in an extreme distortion of the whole geometry around the metal.

Our preliminary studies show that the rhenium(V) complexes of type **2b−d** are catalytically active in olefin oxidation.

In a standard reaction *cis*-cyclooctene was oxidized at 50 °C with *tert*-butyl hydroperoxide in $CHCl_3$ in the presence of **2b−d**. Typically, a solution of 9 mmol of *cis*-cyclooctene, 9 μmol (1 mol %) of the catalyst, and 7.7 mmol dibutyl ether (as internal standard) in 20 mL of $CHCl_3$ was heated at 50 °C and stirred magnetically. The oxidant *tert*-butyl hydroperoxide (1 equiv relative to the olefin) was added at once. The conversion of the olefin and the yield of its epoxide are summarized in Table 2. The resulting epoxide reacts slowly to 2-*tert*-butoxycyclohexanol as a result of ring opening. First studies show an induction period of 50−70 min, during which time no catalytic activity is observed. We assume that the catalytically active species are formed by reaction of the rhenium(V) complexes with *tert*-butyl hydroperoxide. As a slow initial step a ligand dissociation process may create a free coordination site for the adduct formation. Obviously, an oxidation of the rhenium(V) center takes place because finally perrhenate can be isolated. Nevertheless, the active species formed in the induction period could not be characterized yet. Further work on the development of this catalytic system for the oxidation of unfunctionalized olefins is in progress.

Conclusion

Tetradentate Schiff base ligands of the sal_2en type do not coordinate in *all*-equatorial positions in octahedral rhenium(V) complexes of formula ReOCl(L) (C_s symmetry). They rather form asymmetric complexes of C_1 symmetry with an asymmetric coordination of the two *N,O*-units. This situation is different from what is known for Tc(V) and the Mn(III) complexes MnCl(L); the latter are being used in asymmetric olefin epoxidation. Nevertheless, our Re(V) complexes are potential candidates for asymmetric catalysis.

Acknowledgment. This work was supported by the *Deutsche Forschungsgemeinschaft*. We are grateful to R. Schmid for recording 2D NMR spectra.

Supporting Information Available: Tables of hydrogen atom parameters, complete bond distances and bond angles, and anisotropic displacement parameters for **2a−c** (24 pages). Ordering information is given on any current masthead page.

IC9508278

---

(24) Banbery, H. J.; McQuillan, F.; Hamor, T. A.; Jones, C. J.; McCleverty, J. A. *J. Chem. Soc., Dalton Trans.* **1989**, 1405.

(25) Banbery, H. J.; McQuillan, F.; Hamor, T. A.; Jones, C. J.; McCleverty, J. A. *Polyhedron* **1989**, *8*, 5591.

(26) (a) Gilli, G.; Sacerdoti, M.; Bertolasi, V. *Acta Crystallogr.* **1982**, *B38*, 100. (b) Casiraghi, G.; Casnati, G.; Puglia, G.; Sartori, G.; Terenghi, G. *J. Chem. Soc., Perkin Trans. 1* **1980**, 1862.