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Synthesis and Characterization of Unusual Oxidorhenium(V) Cores

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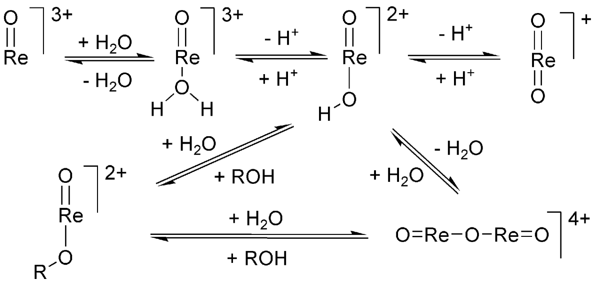
Keywords: Rhenium / Oxido cores / Bridging ligands / Coordination modes

Reactions of $(NBu_4)[ReOCl_4]$ with *N*-(*N''*,*N''*-dialkylaminothiocarbonyl)-*N'*-(2-hydroxyphenyl)benzamidines (H_2L^1) give complexes of the compositions $[ReOCl(L^1)]$ (**1**), *cis*-$[ReO(L^1)(OMe)]$ (**2**), or *cis*,*cis*-$[\{ReO(L^1)\}_2O]$ (**3**) depending on the conditions applied. Compound **3** contains a bridging oxygen atom in the *cis* position to the terminal oxido ligands of both rhenium atoms. The analogous dimeric, sulfur-bridged compound $[\{ReO(L^1)\}_2S]$ (**4**) was obtained by the reaction of **1** with Na_2S.

Introduction

Besides a considerable number of nitrido and imido compounds, the coordination chemistry of rhenium in higher oxidation states is dominated by oxido complexes.[1] They appear in a number of cores, such as $\{ReO\}^{3+}$, $\{ReO(OR)\}^{2+}$,$\{ReO_2\}^{+}$ or $\{Re_2O_3\}^{4+}$, which are related to each other by protonation/deprotonation and/or hydrolysis/condensation reactions (Scheme 1). Thus, rhenium oxido cores are remarkably flexible and form stable complexes with ligands of various steric and electronic demands. The different central units provide optimal charge compensation depending on the net charge of the ligands applied. The fact that incoming alkoxido ligands are almost exclusively directed to the *trans* position of a terminal oxido ligand deserves particular attention. Such a bonding mode is stabilized by a considerable transfer of electron density into the Re–OR bond.[2] Of the 51 structurally characterized Re^V oxido/(monodentate) alkoxido complexes, 43 follow this feature,[3] whereas the alkoxido ligands in the few exceptions have strongly restricting coligands or the rhenium atom has more than one RO^- ligand in its coordination sphere.[4]

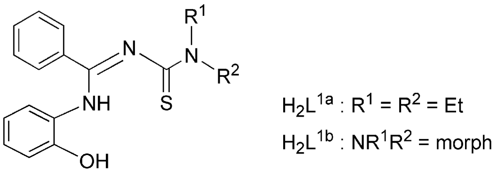


Scheme 1. Common oxidorhenium(V) cores.

Bridging sulfido ligands are extremely rare in the chemistry of oxidorhenium(V) complexes,[5] In some examples, they are accidentally formed by the decomposition of sulfur-containing ligands. This has also been observed for reactions with dialkylaminothiocarbonylbenzamidines, the ligands under study in this report.[6]

Despite the fact that numerous bidentate dialkylaminothiocarbonylbenzamidines have been synthesized and their coordination chemistry is well explored,[7] tridentate representatives of this ligand class are rare and first reports about their coordination behavior with rhenium and technetium cores were only recently published.[8–12] Some of the new rhenium compounds show promising cytotoxic effects against breast cancer cells,[12] whereas an extension of the ligand backbone may give access to multidentate ligand systems with the potential for bioconjugation.[8]

The present report describes some reactions of the neutral Re^V complex, $[ReOCl(L^1)]$ [H_2L^1 = *N*-(*N''*,*N''*-dialkylaminothiocarbonyl)-*N'*-(2-hydroxyphenyl)benzamidines] (Scheme 2), which give access to unusual ligand arrangements, such as *cis*-oxido/alkoxido coordination, *cis*,*cis*-oxido bridges, or sulfido-bridged oxido compounds.



Scheme 2. Chelating ligands used in this work.

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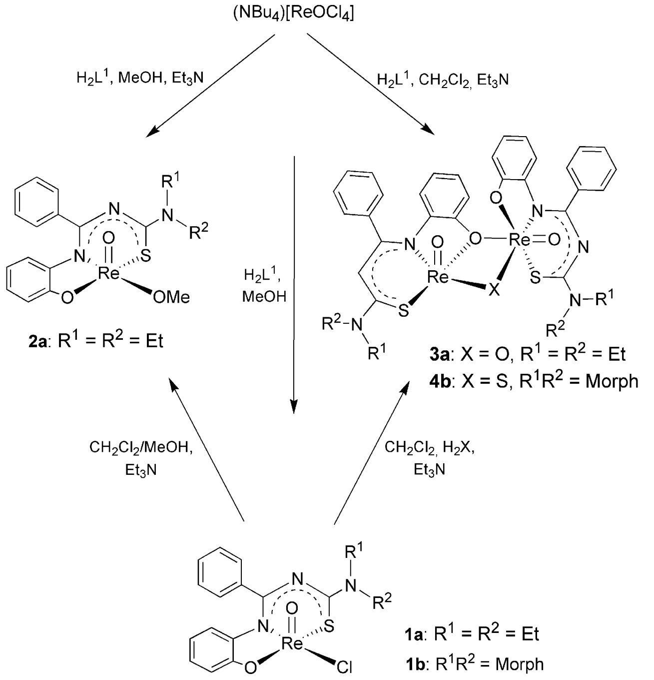
Results and Discussion

Reactions between H_2L^1 ligands and the common Re^V starting material $(NBu_4)[ReOCl_4]$ proceed in different ways depending on the solvents used and the reaction conditions applied. In the absence of a supporting base, $(NBu_4)[ReOCl_4]$ reacts with an equivalent amount of H_2L^1 in MeOH to give red complexes of the composition $[ReOCl(L^1)]$ (**1**); the molecular structures and spectroscopic behavior of which have been previously reported.[8] When a similar reaction is undertaken in hot MeOH and in the presence of a supporting base, such as Et_3N, red solids of the composition $[ReO(OMe)(L^1)]$ (**2**) are obtained in excellent yields. Compound **2** is also quantitatively formed by the addition of Et_3N to a solution of **1** in a refluxing mixture of CH_2Cl_2/MeOH (1:1). More interestingly, the dimeric compounds of the composition $[\{ReO(L^1)\}_2O]$ (**3**), can be isolated in high yield from the reaction of H_2L^1 and $(NBu_4)[ReOCl_4]$ in refluxing CH_2Cl_2 after the addition of Et_3N. The formation of dimeric oxido-Re^V compounds with bridging oxygen atoms is usually explained by the intermediate conversion of the corresponding chloro compounds into hydroxido intermediates and their subsequent condensation.[13] In the present case, however, all our attempts to isolate the intermediate hydroxido species $[ReO(OH)(L^1)]$ failed. Nevertheless, complex **3** was synthesized by the addition of a base to refluxing solutions of **1** in wet CH_2Cl_2. Thus, complex **1**, with its labile chloro ligand, may be regarded as the key compound in the reaction pattern between H_2L^1 and $(NBu_4)[ReOCl_4]$, and compounds **2** and **3** are products of the solvolysis (and condensation) of this complex (Scheme 3).



Scheme 3. Reactions of (NBu_4) $[ReOCl_4]$ with H_2L^1.

The infrared spectrum of $[ReO(OMe)(L^{1a})]$ exhibits a strong absorption of the Re=O vibration at 995 cm^{-1}, which is in the same region of that in $[ReOCl(L^{1a})]$ and in other square-pyramidal oxidorhenium(V) complexes,[2] and far too high for a $\{O{=}Re{-}OR\}^{2+}$ core.[14] The X-ray structure analysis confirms that the rhenium atom in **2** is five-coordinate and the methanolato ligand is *cis* coordinated to the terminal oxido ligand (Figure 1). Selected bond lengths and angles are given in Table 1. An ellipsoid plot and more bonding parameters are given in the Supporting Information.

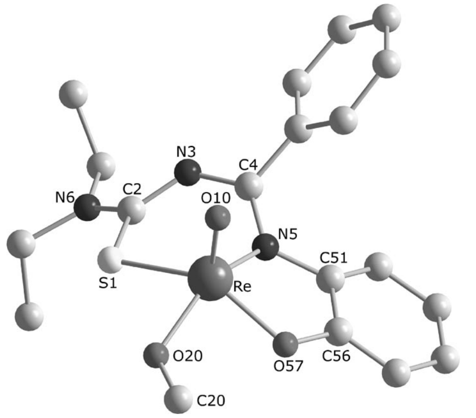


Figure 1. Molecular structure of $[ReO(OMe)(L^{1a})]$ (**2**).[14] Hydrogen atoms have been omitted for clarity.

Table 1. Selected bond lengths [Å] and angles [°] in **2**.

Re–O10	1.692(5)	Re–O57	1.963(5)
Re–O20	2.000(6)	Re–S1	2.289(2)
Re–N5	2.010(6)	C2–N6	1.321(8)
O10–Re–O57	113.0(2)	O10–Re–N5	107.6(3)
O10–Re–S1	108.7(2)	O10–Re–O20	107.5(2)
N5–Re–O20	144.7(2)	S1–Re–O57	138.2(2)

The basal plane of the distorted square pyramid is defined by the donor atoms of the tridentate ligand and the methoxido ligand, whereas the oxido ligand forms its apex. The rhenium atom is placed 0.678(2) Å above the equatorial plane towards O10. The methoxido ligand in the *cis* position to the oxido ligand is an uncommon feature for oxido/alkoxido rhenium complexes. The preferred *trans* coordination is supported by considerable transfer of electron density from the Re=O bond into the Re–alkoxido bond, which leads to bond lengths that are significantly shorter than Re–O single bonds.[3,15] In the bonding situation of **2**, however, the Re–O20 distance of 2.000(6) Å is in the typical range of a rhenium–oxygen single bond.

Complex **3** is soluble in $CHCl_3$ or CH_2Cl_2 and single crystals suitable for X-ray diffraction were obtained by the slow evaporation of a CH_2Cl_2 solution of the complex. The molecular structure of **3** (Figure 2) revealed a dimeric form, in which each oxidorhenium(V) core is coordinated by a tridentate $\{L^{1a}\}^{2-}$ ligand as was discussed for **2**; two such units are connected by one additional oxido ligand and the phenolato oxygen atom of one of the subunits. This results in a dimeric compound consisting of one pentacoordinate subunit and a six-fold coordinated rhenium atom. To the best of our knowledge, there is no precedent for such a coordination mode in which only one bridging oxido ligand is in *cis* position to two terminal ones. Selected bond lengths and angles are given in Table 2. Ellipsoid plots and more details about the molecular structure of **3** are summarized in the Supporting Information.

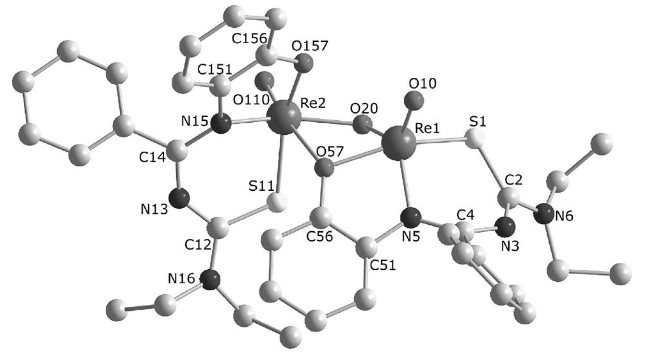


Figure 2. Molecular structure of $[\{ReO(L1^{a})\}_2O]$ (**3**).[14] Hydrogen atoms have been omitted for clarity.

Table 2. Selected bond lengths [Å] and angles [°] in **3** and **4**.

	3	4
Re1–O10	1.65(1)	1.675(8)
Re1–S1	2.314(4)	2.297(3)
Re1–N5	1.98(1)	2.023(8)
Re1–O57	2.030(8)	2.009(6)
Re1–O20	1.87(1)	–
Re1–S20	–	2.281(3)
Re2–O110	1.67(1)	1.651(8)
Re2–S11	2.298(5)	2.286(3)
Re2–N15	1.99(1)	2.029(7)
Re2–O157	1.99(1)	1.971(8)
Re2–O20	1.992(9)	–
Re2–S20	–	2.411(3)
Re2–O57	2.52(1)	2.672(6)
O10–Re1–O20/S20	123.6(5)	109.9(3)
O110–Re2–O20/S20	107.9(4)	99.8(3)
O10–Re1–O57	104.2(5)	107.5(3)
O110–Re2–O157	104.0(5)	106.8(4)
O10–Re1–N5	112.1(6)	112.5(4)
O110–Re2–N15	106.2(5)	107.8(3)
O10–Re1–S1	100.5(4)	107.2(3)
O110–Re2–S11	101.5(4)	104.6(3)
O110-Re2–O57	173.0(4)	167.3(1)
Re1–O20/S20-Re2	118.5(4)	104.8(1)
Re1–O57–Re2	92.9(4)	104.4(1)

The coordination planes of the chelating ligands in **3** are almost perpendicular to each other and the Re1–O20–Re2 angle is 118.5(4)°. Such a situation goes along with a lower double bond character in the bent oxido bridge compared to a linear one, which is also reflected by the Re–O20 bond lengths of 1.867(10) and 1.992(9) Å for Re1 and Re2, respectively. The distance between Re2 and O57 of 2.52(1) Å is significantly longer than a rhenium–oxygen single bond and reflects a weak interaction, which is confirmed by spectroscopic studies in solution. The ^{1}H NMR spectrum of **3** in $CDCl_3$ at 20 °C shows that the two coordinated $\{L^{1a}\}^{2-}$ ligands are magnetically equivalent. This indicates free rotation around the Re1–O20–Re2 bonds and, consequently, no considerable interaction between Re2 and O57 is detected in solution.

A similar reaction between $(NBu_4)[ReOCl_4]$ and two equivalents of H_2L^{1b} in a refluxing CH_2Cl_2/acetone mixture, after the addition of NEt_3, resulted in the isolation of two compounds: the expected major product $[\{ReO(L^{1b})\}_2O]$ and a small amount of red crystals of $[\{ReO(L^{1b})\}_2S]$ (**4**). The formation of a bridging sulfur atom can be explained by the reaction of the intermediate compound $[ReOCl(L^{1b})]$ with S^{2-}, which is generated by the gradual decomposition of H_2L^{1b}. Similar decomposition reactions of dialkylthiocarbamoyl benzamidines and the formation of a sulfido-bridged dimer have been reported recently for phenylimido rhenium(V) complexes under similar conditions.[6]

A more rational synthesis of **4** is given with the reaction of $[ReOCl(L^{1b})]$ with an equivalent amount of $Na_2S \cdot 9\ H_2O$ in CH_2Cl_2/acetone. Red crystals of **4** are obtained in yields between 15 and 20%, in addition to an uncharacterized red oil, which could not be solidified.

The molecular structure of **4** (Figure 3) reveals an analogous bonding pattern to that discussed for **3**. The bond length between the rhenium atom and the bridging sulfur atom in the square-pyramidal unit is shorter by approximately 0.13 Å than that in the octahedral unit. As a consequence of the sulfido bridge, the Re2–O57 distance in **4** is 2.672(6) Å. A comparison of selected bond lengths and angles for compounds **3** and **4** is given in Table 2 and more structural parameters together with ellipsoid representations are provided in the Supporting Information.

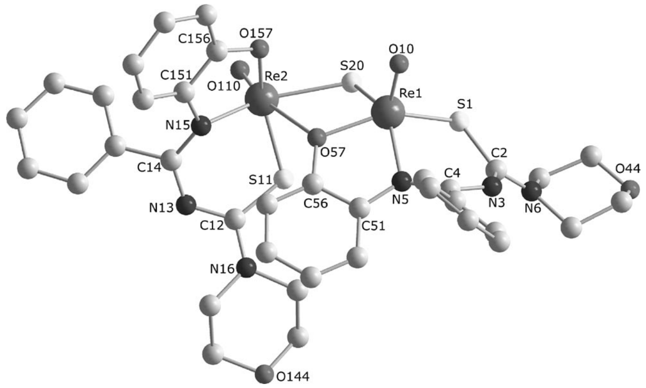
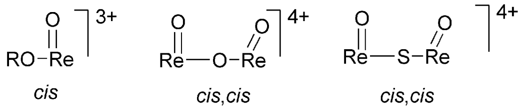


Figure 3. Molecular structure of $[\{ReO(L^{1b})\}_2S]$ (**4**).[14] Hydrogen atoms have been omitted for clarity.

As discussed for **3**, the interactions between Re2 and O57 are not strong enough to maintain this arrangement in solution. This is evidenced by the detection of two magnetically equivalent units in the NMR spectroscopic experiments.

Conclusion

Each of the compounds **2**, **3** and **4** represent a rare or hitherto unknown structural feature in the coordination chemistry of rhenium: *cis*-oxido/alkoxido coordination, *cis,cis*-oxido/oxido bridges, or *cis,cis*-oxido/sulfido bridges as is summarized in Scheme 4. The main reason for the uncommon structural features is the stable meridional coordination of the tridentate ligand in the equatorial sphere of a monooxido unit. This restrains the synthetic flexibility of the fragment in secondary ligand exchange reactions and allows access to unusual cores. Such an approach may serve as model for the synthesis of other unusual oxidometallate structures.



Scheme 4. Oxidorhenium(V) cores discussed in this paper.

Experimental Section

Materials: All reagents used in this study were reagent grade and used without further purification. Solvents were dried and freshly distilled prior to use unless otherwise stated. $(NBu_4)[ReOCl_4]$,[16] H_2L^{1a},[8] HL^{1b},[8] and $[ReOCl(L^1)]$ (**1**)[8] were synthesized by previously published procedures.

Physical Measurements: Infrared spectra were measured as KBr pellets on a Shimadzu FTIR spectrometer between 400 and 4000 cm^{-1}. FAB$^+$ mass spectra were recorded with a TSQ (Finnigan) instrument using a nitrobenzyl alcohol matrix. Positive ESI mass spectra were measured with an Agilent 6210 ESI-TOF (Agilent Technologies). All MS results are given in the form: *m*/*z*, assignment. Elemental analysis of carbon, hydrogen, nitrogen, and sulfur were determined using a Heraeus vario EL elemental analyzer. NMR spectra were measured using a JEOL 400 MHz multinuclear spectrometer.

Syntheses of Complexes

$[ReO(OMe)(L^{1a})]$ (2): Method 1. H_2L^{1a} (0.1 mmol) was dissolved in MeOH (5 mL) and $(NBu_4)[ReOCl_4]$ (58 mg, 0.1 mmol) was added. After adding Et_3N (3 drops), the reaction mixture was heated under reflux for 30 min. The red precipitate was filtered off, washed with cold methanol, and recrystallized from CH_2Cl_2/MeOH; yield 47 mg (85%).

Method 2: $[ReOCl(L^{1a})]$ (56 mg, 0.1 mmol) was suspended in MeOH (5 mL) and Et_3N (3 drops) was added. The reaction mixture was heated under reflux for 15 min. After being cooled to room temperature, the red solid was filtered off, washed with cold MeOH, and dried under vacuum; yield 90% (50 mg). $C_{19}H_{22}N_3O_3ReS$ (558.66): calcd. C 40.85, H 3.97, N 7.52, S 5.74; found C 40.71, H 3.84, N 7.52, S 5.53. IR (KBr): $\tilde{\nu}$ = 3060 (w), 2977 (w), 2866 (w), 1535 (s), 1473 (s), 1447 (w), 1358 (s), 1319 (m), 1246 (s), 1142 (w), 1076 (w), 995 (s), 772 (m), 691 (s), 671 (m) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.34 (m, 6 H, CH_3), 3.31 (s, 3 H, OMe) 3.82 (m, 2 H, CH_2), 4.24 (m, 1 H, CH_2), 4.40 (m, 1 H, CH_2), 6.5–6.6 (m, 2 H, PhOH), 6.84 (t, J = 7.6 Hz, 1 H, PhOH), 7.29 (d, J = 7.5 Hz, 1 H, PhOH), 7.37 (t, J = 7.4 Hz, 2 H, Ph), 7.45 (t, J = 7.3 Hz, 1 H, Ph), 7.67 (d, J = 7.3 Hz, 2 H, Ph) ppm. ESI$^+$ MS: *m*/*z* (%) = 560 (100) $[M + H]^+$, 582 (60) $[M + Na]^+$.

$[\{ReO(L^{1a})\}_2O]$ (3): $[ReOCl(L^{1a})]$ (56 mg, 0.1 mmol) was dissolved in CH_2Cl_2 (3 mL) and Et_3N (1 drop) was added. The mixture was heated under reflux for 15 min. The solvent was then removed under vacuum and the residue crystallized from a CH_2Cl_2/n-hexane mixture to give dark red crystals; yield 53 mg (50%). $C_{36}H_{38}N_6O_5Re_2S_2$ (1071.14): calcd. C 40.36, H 3.58, N 7.84, S 5.99; found C 40.02, H 3.37, N 7.68, S 5.85. IR (KBr): $\tilde{\nu}$ = 3055 (w), 2980 (w), 2928 (w), 1516 (s), 1484 (s), 1435 (m), 1342 (w), 1026 (m), 970 (s), 779 (m), 691 (w). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.39 (m, 6 H, CH_3), 3.8–4.2 (m, 4 H, CH_2), 6.29 (t, J = 7.1 Hz, 1 H, PhOH), 6.42 (d, J = 7.2 Hz, 1 H, PhOH), 6.65 (m, 2 H, PhOH), 7.29 (t, J = 7.3 Hz, 2 H, Ph), 7.34 (t, J = 7.4 Hz, 1 H, Ph), 7.68 (d, J = 7.3 Hz, 2 H, Ph) ppm. ESI$^+$ MS: *m*/*z* = 1072.1387, 70, $[M + H]^+$; 1095.1397, 100, $[M + Na]^+$; 1111.1123, 50, $[M + K]^+$.

$[\{ReO(L^{1b})\}_2S]$ (4): $Na_2S\cdot 9H_2O$ (0.24 mg, 0.1 mmol) and Et_3N (1 drop) were added to a solution of $[ReOCl(L^{1b})]$ (56 mg, 0.1 mmol) in CH_2Cl_2/acetone (1:1; 3 mL) and the mixture heated under reflux for 30 min. After complete removal of the solvent, the residue was crystallized from $CH_2Cl_2/CHCl_3$ to give dark red crystals; yield 17 mg (15%). $C_{36}H_{34}N_6O_6Re_2S_3$ (1115.07): calcd. C 38.77, H 3.07, N 7.54, S 8.63; found C 38.49, H 3.19, N 7.44, S 8.63. IR (KBr): $\tilde{\nu}$ = 2954 (w), 2916 (w), 2850 (w), 1542 (s), 1523 (s), 1473 (s), 1438 (m), 1353 (w), 1245 (m), 1114 (w), 1022 (m), 972 (s), 752 (m), 686

Table 3. Crystal data and details of the structure determinations.

	2	**3**·1/2CH_2Cl_2	**4**·2CH_2Cl_2
Formula	$C_{19}H_{22}N_3O_3ReS$	$C_{36.50}H_{39}ClN_6O_5Re_2S_2$	$C_{38}H_{38}Cl_4N_6O_6Re_2S_3$
M_w	558.66	1113.71	1285.12
Crystal system	monoclinic	monoclinic	monoclinic
a [Å]	8.668(1)	14.923(1)	10.273(1)
b [Å]	13.159(1)	18.166(1)	16.045(1)
c [Å]	17.152(1)	15.381(1)	13.202(1)
α [°]	90	90	90
β [°]	91.90(1)	97.24(1)	96.57(1)
γ [°]	90	90	90
V [Å^3]	1955.3(3)	4136.3(4)	2161.7(3)
Space group	$P2_1/n$	$P2_1/n$	$P2_1$
Z	4	4	2
$D_{calcd.}$ [g cm^{-3}]	1.898	1.788	1.974
μ [mm^{-1}]	6.346	6.060	6.040
Number of reflections	13201	16012	19178
Number of independent reflections	5236	7080	11454
Number of parameters	245	490	532
R_1 / wR_2	0.0386 / 0.1129	0.0633 / 0.0878	0.0508 / 0.0758
GOF	0.929	0.857	0.820
Flack parameter	–	–	–0.003(9)

(w). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.54 (m, 1 H, NCH_2), 3.70 (m, 2 H, NCH_2), 3.83 (m, 2 H, NCH_2 + OCH_2), 4.21 (m, 1 H, OCH_2), 4.28 (m, 1 H, OCH_2), 4.45 (m, 1 H, OCH_2), 6.30 (t, J = 7.4 Hz, 1 H, PhOH), 6.45 (d, J = 7.2 Hz, 1 H, PhOH), 6.61 (m, 2 H, PhOH), 7.29 (t, J = 7.5 Hz, 2 H, Ph), 7.37 (t, J = 7.4 Hz, 1 H, Ph), 7.64 (d, J = 7.3 Hz, 2 H, Ph) ppm. ESI$^+$ MS: m/z = 1116.0706, 60, $[M + H]^+$; 1139.0768, 100, $[M + Na]^+$.

X-ray Crystallography: The intensities for the X-ray crystallographic determinations were collected on a STOE IPDS 2T instrument with Mo-K_α radiation (λ = 0.71073 Å). Standard procedures were applied for data reduction and absorption correction. Structure solution and refinement were performed with SHELXS97 and SHELXL97.[17] Hydrogen atom positions were calculated for idealized positions and treated with the "riding model" option of SHELXL.

A disorder was refined for two carbon atoms of one of the ethyl residues in compound **3**. Two parts are refined with occupation percentages of 66/34. More details on data collections and structure calculations are contained in Table 3.

CCDC-783427 (for **2**), CCDC-783428 (for **3**·1/2CH_2Cl_2), and CCDC-783429 (for **4**·2CH_2Cl_2) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see also the footnote on the first page of this article): Crystallographic structure determination parameters, ellipsoid plots, and tables with bond lengths and angles.

Acknowledgments

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[1] U. Abram, *Rhenium*, in: *Comprehensive Coordination Chemistry II* (Eds.: J. A. McCleverty, T. J. Mayer), Elsevier, Amsterdam, The Netherlands, **2003**, vol. 5, p. 271.

[2] a) A. Paulo, A. Domingos, J. Marcalo, A. Pires de Matos, I. Santos, *Inorg. Chem.* **1995**, *34*, 2113; b) H. Braband, O. Blatt, U. Abram, *Z. Anorg. Allg. Chem.* **2006**, *632*, 2251.

[3] *Cambridge Structural Database*, version 5.31, **2009**, The Cambridge Crystallographic Data Centre, Cambridge, U. K.

[4] a) A. Paulo, J. Ascenso, A. Domingos, A. Galvao, I. Santos, *J. Chem. Soc., Dalton Trans.* **1989**, 1293; b) C.-M. Che, Y.-P. Wang, K.-S. Yeung, K. Yin Wong, S. Ming Peng, *J. Chem. Soc., Dalton Trans.* **1992**, 2675; c) G. A. Seisenbaeva, A. V. Shevelkov, J. Tegenfeldt, L. Kloo, D. V. Drobot, V. G. Kessler, *J. Chem. Soc., Dalton Trans.* **2001**, 2762; d) D. Nunes, A. Domingos, A. Paulo, M. F. N. N. Carvalho, A. J. L. Pombeiro, *Inorg. Chim. Acta* **1998**, *271*, 65; e) J. D. C. Correia, A. Domingos, I. Santos, C. Bolzati, F. Refosco, F. Tisato, *Inorg. Chim. Acta* **2001**, *315*, 213; V. G. Kessler, G. A. Seisenbaeva, A. V. Shevelkov, G. V. Khvorykh, *J. Chem. Soc., Chem. Commun.* **1995**, 1779.

[5] a) J. Jacob, I. A. Guzei, J. H. Espenson, *Inorg. Chem.* **1999**, *38*, 3266; b) W. A. Herrmann, K. A. Jung, E. Herdtweck, *Chem. Ber.* **1989**, *122*, 2041; c) S. Cai, D. M. Hoffmann, D. A. Wierda, *Inorg. Chem.* **1991**, *30*, 827.

[6] B. Kuhn, U. Abram, *Z. Anorg. Allg. Chem.* **2008**, *634*, 2982.

[7] a) J. Hartung, G. Weber, L. Beyer, R. Szargan, *Z. Anorg. Allg. Chem.* **1985**, *523*, 153; b) R. del Campo, J. J. Criado, E. Garcia, M. R. Hermosa, A. Jimenez-Sanchez, J. L. Manzano, E. Monte, E. Rodriguez-Fernandez, F. Sanz, *J. Inorg. Biochem.* **2002**, *89*, 74; c) W. Hernandez, E. Spodine, R. Richter, K.-H. Hallmeier, U. Schröder, L. Beyer, *Z. Anorg. Allg. Chem.* **2003**, *629*, 2559; d) U. Schröder, R. Richter, L. Beyer, J. Angulo-Cornejo, M. Lino-Pacheco, A. Guillen, *Z. Anorg. Allg. Chem.* **2003**, *629*, 1051.

[8] H. H. Nguyen, J. Grewe, J. Schroer, B. Kuhn, U. Abram, *Inorg. Chem.* **2008**, *47*, 5136.

[9] H. H. Nguyen, U. Abram, *Polyhedron* **2009**, *8*, 3945.

[10] H. H. Nguyen, P. I. da S. Maia, V. M. Deflon, U. Abram, *Inorg. Chem.* **2009**, *48*, 25.

[11] H. H. Nguyen, V. M. Deflon, U. Abram, *Eur. J. Inorg. Chem.* **2009**, *21*, 3179.

[12] H. H. Nguyen, J. J. Jegathesh, P. I. da S. Maia, V. M. Deflon, R. Gust, S. Bergemann, U. Abram, *Inorg. Chem.* **2009**, *48*, 9356.

[13] a) L. Hansen, E. Alessio, M. Iwamoto, P. A. Marzilli, L. G. Marzilli, *Inorg. Chim. Acta* **1995**, *240*, 413; b) N. P. Johnson, F. I. M. Taha, G. Wilkinson, *J. Chem. Soc.* **1964**, 2614.

[14] K. Brandenburg, H. Putz, *DIAMOND – A program for the visualization of molecular structures*, vers. 3.2.

[15] S. Abram, U. Abram, E. Schulz Lang, J. Strähle, *Acta Crystallogr., Sect. C* **1995**, *51*, 1078, and references cited therein.

[16] R. Alberto, R. Schibli, A. Egli, P. A. Schubiger, W. A. Herrmann, G. Artus, U. Abram, T. Kaden, *J. Organomet. Chem.* **1995**, *217*, 492.

[17] G. M. Sheldrick, *SHELXS-97* and *SHELXL-97*, *Programs for the Solution and Refinement of Crystal Structures*, University of Göttingen, Göttingen, Germany, **1997**.

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