590 Inorg. Chem. 2011, 50, 590–596
DOI: 10.1021/ic1017642

Inorganic Chemistry
Article

Bipodal Acylthiourea Ligands as Building Blocks for Bi-, Tetra-, and Polynuclear Oxorhenium(V) Complexes

Hung Huy Nguyen,*,[†] Pham Chien Thang,[†] Axel Rodenstein,[‡] Reinhard Kirmse,[‡] and Ulrich Abram*,[§]

[†] *Department of Chemistry, Hanoi University of Science, 19 Le Thanh Tong, Hanoi, Vietnam,*
[‡] *Institute of Inorganic Chemistry, University of Leipzig, Johannisallee 29, D-04103 Leipzig, Germany, and*
[§] *Institute of Chemistry and Biochemistry, Freie Universität Berlin, Fabeckstrasse 34-36,*
D-14195 Berlin, Germany

Received August 30, 2010

Reactions of $(NBu_4)[ReOCl_4]$ and 3,3,3′,3′-tetraalkyl-1,1′-isophthaloylbis(thioureas), $H_2phth(R_2tu)_2$ where R = Et, *i*-Bu, in hot MeOH with the addition of Et_3N give red products of the composition $[ReO(OMe)\{phth(R_2tu)_2\}]_2$ (**8a**, R = Et; **8b**, R = *i*-Bu). X-ray structures of **8** reveal symmetric binuclear complexes containing two almost coplanar organic ligands, each of which coordinates to two rhenium centers via the two bidentate-O,S moieties. The octahedral coordination spheres of the rhenium atoms are completed by each one oxo and one methoxido ligand which are directed perpendicular to the plane defined by the $\{phth(R_2tu)_2\}^{2-}$ ligands. While in **8a**, both methoxido ligands point to the same side of the described plane and form a *syn* isomer, the MeO^- ligands in **8b** are located at opposite sides and form an *anti* isomer. Studies in solution show that there exists a reversible equilibrium between the *anti* and *syn* isomers. Dimerization/condensation of complexes **8** with the formation of tetranuclear complexes of the composition $[\{ReO\{phth(R_2tu)_2\}\}_2O]_2$ (**9**) and/or polynuclear species is observed in solutions, which do not contain MeOH.

Introduction

1,1-Dialkylbenzoylthioureas (**1**) are well-known as classical S,O bidentate ligands, which form stable chelates with almost all transition metals.[1] Most of the examples refer to complexes with d^8 and d^9 transition metal ions, where the formation of *cis* square-planar complexes is preferred.[2] Relatively less, however, is known about the coordination chemistry of bipodal acylthiourea derivatives.[3−5] This is surprising because symmetrical bipodal derivatives with two S,O chelating moieties such as 3,3,3′,3′-tetraalkyl-1,1′-phenylenedicarbonyl bis(thioureas) are best suitable for synthesis of multinuclear complexes. Particularly, *meta*-substituted phthaloylbis(thiourea) ligands, $H_2phth(R_2tu)_2$ are able to form “self-assembled” metallamacrocyclic complexes of the composition $[M\{(phth(R_2tu)_2\}]_2$ (**2**), as has been demonstrated for metal ions such as Cu^{2+}, Ni^{2+}, Pd^{2+}, and Pt^{2+}.[4,5] In all structurally characterized binuclear complexes of this type, the original coordination motif of the bidentate benzoylthioureas, square-planar coordination spheres with *cis* arrangement of the donor atoms, is maintained.[5] The almost planar, binuclear complexes can be polymerized to infinite chains by reactions with exobidonor linkers such as pyrazine, 4,4′-bipyridine, 1,2-di(4-pyridyl)ethane, or

---

*To whom correspondence should be addressed. Phone: (#49) 30 83854002. Fax: (#49) 30 83852676. E-mail: abram@chemie.fu-berlin.de.

[1] (a) Beyer., L.; Hoyer, E.; Liebscher, J.; Hartmann, H. *Z. Chem.* **1981**, *21*, 228. (b) Koch, K. R. *Coord. Chem. Rev.* **2001**, *216−217*, 473. (c) Beyer, L.; Hoyer, E.; Hennig, H.; Kirmse, R.; Hartmann, H.; Liebscher, J. *J. Prakt. Chem.* **1975**, *317*, 829. (d) Schmidt, S.; Dietze, F.; Hoyer, E. *Z. Anorg. Allg. Chem.* **1991**, *603*, 33. (e) Mohamadou, A.; Dechamps-Olivier, I.; Barbier, J. P. *Polyhedron* **1994**, *13*, 1363. (f) del Campo, R.; Criado, J. J.; Gheorghe, R.; Gonzalez, F. J.; Hermosa, M. R.; Sanz, F.; Manzano, J. L.; Monte, E.; Rodriguez-Fernandez, E. *J. Inorg. Biochem.* **2004**, *98*, 1307.

[2] (a) del Campo, R.; Criado, J. J.; Garcia, E.; Hermosa, M. R.; Jimenez-Sanchez, A.; Manzano, J. L.; Monte, E.; Rodriguez-Fernandez, E.; Sanz, F. *J. Inorg. Biochem.* **2002**, *89*, 74. (b) Emen, F. M.; Flörke, U.; Külcü, N.; Arslan, H. *Acta Crystallogr.* **2003**, *E59*, m582. (c) Arslan, H.; Flörke, U.; Külcü, N. *Z. Kristallogr., New Cryst. Struct.* **2004**, *219*, 409. (d) Arslan, H.; Vanderveer, D.; Emen, F.; Külcü, N. *Z. Kristallogr., New Cryst. Struct.* **2003**, *218*, 479. (e) Fitzl, G.; Beyer, L.; Sieler, J.; Richter, R.; Kaiser, J.; Hoyer, E. *Z. Anorg. Allg. Chem.* **1977**, *433*, 237. (f) Irving, A.; Koch, K. R.; Matoetoe, M. *Inorg. Chim. Acta* **1993**, *206*, 193. (g) Sacht, C.; Datt, M. S.; Otto, S.; Roodt, A. *J. Chem. Soc., Dalton Trans.* **2000**, 727. (h) Arslan, H.; Külcü, N.; Flörke, U. *Trans. Met. Chem.* **2003**, *28*, 816. (i) Schröder, U.; Richter, R.; Anguio-Conejo, J.; Lino-Pacheco, M.; Gullien, A. *Z. Anorg. Allg. Chem.* **2003**, *629*, 1081.

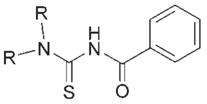
[3] Richter, R.; Sieler, J.; Köhler, R.; Hoyer, E.; Beyer, L.; Leban, I.; Golic, L. *Z. Anorg. Allg. Chem.* **1989**, *578*, 198.

[4] (a) Rodenstein, A.; Richter, R.; Kirmse, R. *Z. Anorg. Allg. Chem.* **1713**, *2007*, 633. (b) Bourne, S. A.; Hallale, O.; Koch, K. R. *Cryst. Growth Des.* **2005**, *5*, 307. (c) Rodenstein, A.; Griebel, J.; Richter, R.; Kirmse, R. *Z. Anorg. Allg. Chem.* **2008**, *634*, 867.

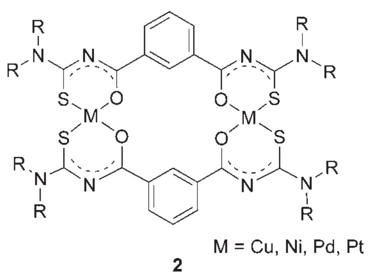
[5] (a) Koch, K. R.; Bourne, S. A.; Coetzee, A.; Miller, J. *J. Chem. Soc., Dalton Trans.* **1999**, *18*, 3157. (b) Koch, K. R.; Hallale, O.; Bourne, S. A.; Miller, J.; Bacsa, J. *J. Mol. Struct.* **2001**, *561*, 185.

[6] Hallale, O.; Bourne, S. A.; Koch, K. R. *New J. Chem.* **2005**, *29*, 1416.

1,2-di(4-pyridyl)ethylene, and the resulting extension of the coordination number of the metal ions from four to six.[6]

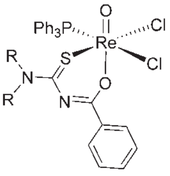


1

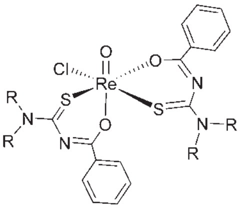


2

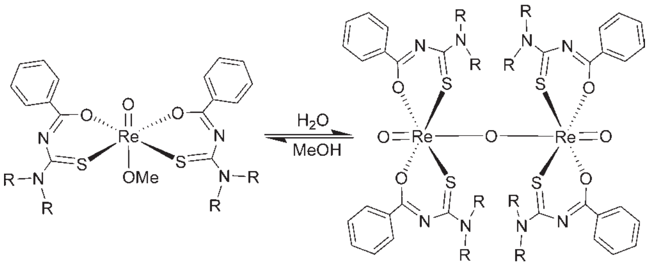
Rhenium and technetium complexes with benzoylthiourea ligands have recently been explored more in detail, and a number of oxorhenium(V) species have been isolated and structurally characterized.[7,8] In addition to complexes with axially (**3**) and axially/equatorially (**4**) coordinated benzoylthioureato ligands, also species with two equatorially coordinated chelating ligands (**5**) could be isolated when the reaction was done in methanol under addition of a supporting base which provides deprotonation of the alcohol.[8] This reveals that the bipodal bis-benzoylthiourea ligands H_2phth(R_2tu)$_2$ should also be suitable for the formation of binuclear planar rhenium methoxido complexes establishing an equatorial coordination sphere similar to the corresponding complexes with the d^8 and d^9 transition metal ions referred above. More interestingly, we found that methoxido complexes of type **5** can reversibly be converted into oxo-bridged dimeric compounds of the composition [{ReO(Et_2btu)$_2$}O] (**6**) under mild conditions.[8] Applying this reaction pattern to rhenium complexes with {Phth(R_2tu)$_2$}$^{2-}$ might give access to three-dimensional metallamacrocyclic compounds.



3



4



5 **6**

Experimental Section

Materials. All reagents used in this study were reagent grade and used without further purification. Solvents were dried and used freshly distilled prior to use unless otherwise stated. (NBu_4)[$ReOCl_4$] was prepared by a standard procedure.[9]

Physical Measurements. Infrared spectra were measured as KBr pellets on a Shimadzu FT-IR-spectrometer between 400 and 4000 cm^{-1}. Electrospray ionization (ESI) mass spectra were measured with an Agilent 6210 ESI-TOF (Agilent Technologies). All mass spectroscopy (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 taken with a JEOL 400 MHz multinuclear spectrometer.

Syntheses. 3,3,3′,3′-Tetraalkyl-1,1′-isophthaloylbis(thioureas). The syntheses of H_2phth(R_2tu)$_2$ were performed by the procedure of Beyer et al.[10]

Data for H_2phth(Et_2tu)$_2$. Anal. Calcd. for $C_{18}H_{26}N_4O_2S_2$: C, 54.79; H, 6.64; N, 14.20; S, 16.25%. Found: C, 54.32; H, 6.61; N, 14.30; S, 16.22%. IR (KBr, cm^{-1}): 3117 (m), 2974 (w), 2935 (w), 2873 (w), 1690 (vs), 1535 (vs), 1427 (vs), 1280 (m), 1215 (vs), 1130 (m), 887 (m), 725 (m). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 1.26 (m, 12H, CH_3), 3.54 (q, 4H, J = 6.8 Hz, CH_2), 3.94 (q, 4H, J = 6.8 Hz, CH_2), 7.49 (t, 1H, J = 7.6 Hz, Ph), 7.94 (d, 2H, J = 7.6 Hz, Ph), 8.22 (s, 1H, Ph), 8.85 (s, 2H, NH).

Data for H_2phth(*i*-Bu_2tu)$_2$. Anal. Calcd. for $C_{26}H_{42}N_4O_2S_2$: C, 61.62; H, 8.35; N, 11.06; S, 12.65%. Found: C, 61.54; H, 8.39; N, 11.15; S, 12.58%. IR (KBr, cm^{-1}): 3232 (m), 2958 (m), 2870 (m), 1686 (vs), 1524 (vs), 1450 (vs), 1415 (vs), 1261 (m), 1215 (vs), 1143 (m), 894 (w), 721 (m). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 0.88 (d, 12H, J = 6.6 Hz, CH_3), 1.02 (d, 12H, J = 6.6 Hz, CH_3), 2.09 (m, 2H, CH), 2.35 (m, 2H, CH), 3.35 (d, 4H, J = 7.6 Hz, CH_2), 3.80 (d, 4H, J = 7.6 Hz, CH_2), 7.60 (t, 1H, J = 7.8 Hz, Ph), 8.04 (d, 2H, J = 7.7 Hz, Ph), 8.31 (s, 1H, Ph), 8.61 (s, 2H, NH).

[ReOCl{phth(R_2tu)$_2$}]$_n$ (7). (NBu_4)[$ReOCl_4$] (58 mg, 0.1 mmol) was dissolved in 3 mL of cold MeOH and H_2phth(R_2tu)$_2$ (0.1 mmol) was added. The reaction mixture was stirred for 15 min at a temperature not higher than 10 °C. The formed green precipitate was filtered off, washed with cold MeOH, and dried in vacuo.

Data for 7a (R = Et). Yield 93% (58.6 mg). Anal. Calcd. for ($C_{18}H_{24}ClN_4O_3ReS_2$)$_n$: C, 34.31; H, 3.84; N, 8.89; S, 10.18%. Found:C, 33.91; H, 3.9; N, 8.29; S, 9,87%. IR (KBr, cm^{-1}): 2974 (m), 2932 (m), 2874 (w), 1593 (m), 1504 (vs), 1435 (vs), 1354 (vs), 1258 (m), 1196 (m), 1142 (m), 1076 (m), 980 (s), 933 (w), 847 (w), 818 (w), 725 (s), 667 (m), 428(w). ESI$^+$ MS in MeOH: *m*/*z* = 595 (5% base peak, [(ReO)L]$^+$), 1221 (30% base peak, [(ReO)$_2$L$_2$(OMe)]$^+$), 1845 (5% base peak, [(ReO)$_3$L$_3$(OMe)$_2$]$^+$), and 2471 (5% base peak, [(ReO)$_4$L$_4$(OMe)$_3$]$^+$.

Data for 7b (R = *i*-Bu). Yield 90% (66.8 mg). Anal. Calcd. for ($C_{26}H_{40}ClN_4O_3ReS_2$)$_n$: C, 42.06; H, 5.43; N, 7.55; S, 8.64%. Found: C, 41.96; H, 5.31; N,6.89; S, 9.28%. IR (KBr, cm^{-1}): 2959 (s), 2870 (m), 1597 (m), 1501 (vs), 1427 (vs), 1357 (vs), 1262 (m), 1238 (m), 1146 (m), 1099 (m), 984 (s), 922 (w), 818 (w), 725 (m), 671 (w), 82 (w), 513 (w). ESI$^+$ MS in MeOH: *m*/*z* = 707 (20% base peak, [(ReO)L]$^+$), 1445 (100% base peak, [(ReO)$_2$L$_2$(OMe)]$^+$), 2183 (10% base peak, [(ReO)$_3$L$_3$(OMe)$_2$]$^+$) and 2190 (5% base peak, [(ReO)$_3$L$_3$Cl$_2$]$^+$.

[ReO(OMe){phth(R_2tu)$_2$}]$_2$ (8). A mixture of (NBu_4)[$ReOCl_4$] (58 mg, 0.1 mmol), H_2phth(R_2tu)$_2$ (0.1 mmol), and 3 drops of Et_3N in MeOH (3 mL) was heated under reflux for 30 min. After cooling to 0 °C, the formed red precipitate was filtered off, washed with cold MeOH, and recrystallized from CH_2Cl_2/MeOH.

Alternatively, compounds **8** can be synthesized by heating suspensions of compounds **7** in MeOH. A supporting base like Et_3N may be added to accelerate the reaction.

Data for 8a (R = Et). Yield 91% (56.9 mg). Anal. Calcd. for $C_{38}H_{54}N_8O_8Re_2S_4$: C, 36.44; H, 4.43; N, 8.95; S, 10.24%.

---

(7) Dilworth, J. R.; Lewis, J. S.; Miller, J. R.; Yifan, Z. *Polyhedron* **1993**, *12*, 221. Abram, U.; Abram, S.; Alberto, R.; Schibli, R. *Inorg. Chim. Acta* **1996**, *248*, 193. Nguyen, H. H.; Abram., U. *Z. Anorg. Allg. Chem.* **2008**, *634*, 1560.

(8) Huy, N. H.; Abram, U. *Inorg. Chem.* **2007**, *46*, 5310.

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

(10) Köhler, R.; Kirmse, R.; Richter, R.; Sieler, J.; Hoyer, E.; Beyer, L. *Z. Anorg. Allg. Chem.* **1986**, *537*, 133.

Table 1. X-ray Structure Data Collection and Refinement Parameters

	syn-**8a**·3CH_2Cl_2	*anti*-**8b**	**9a**	**9b**·2DMSO·2H_2O
formula	$C_{41}H_{54}Cl_6N_8O_8Re_2S_4$	$C_{54}H_{80}N_8O_8Re_2S_4$	$C_{72}H_{96}N_{16}O_{14}Re_4S_8$	$C_{106}H_{164}N_{16}O_{16}Re_4S_9$
M_w	1500.26	1469.90	2410.93	3048.02
crystal system	monoclinic	triclinic	monoclinic	monoclinic
a/Å	27.336(1)	9.219(1)	16.017(1)	19.765(2)
b/Å	8.246(1)	10.346(1)	18.621(1)	15.811(1)
c/Å	25.021(1)	18.489(2)	16.055(1)	23.642(2)
α /deg	90	76.89(1)	90	90
β/deg	96.57(1)	83.20(1)	117.83(1)	92.86(1)
γ/deg	90	64.15(1)	90	90
V/ Å^3	5602.7(7)	1545.3(3)	4234.6(4)	7379.1(9)
space group	$C2/c$	$P\bar{1}$	$P2_1/c$	$P2_1/c$
Z	4	1	2	2
$D_{calc.}$/g cm^{-3}	1.779	1.580	1.891	1.372
μ /mm^{-1}	4.806	4.104	5.966	3.468
no. of reflections	14446	16221	26466	51372
no. of independent	5904	8237	11357	19660
no. parameters	313	344	515	724
R1/wR2	0.0474/0.1401	0.0578/0.1372	0.0650/0.1183	0.1033/0.2286
GOF	0.929	1.008	0.922	0.948

Found: C, 36.75; H, 4.28; N, 8.83; S, 10.02%. IR (KBr, cm^{-1}): 2978 (m), 2935 (w), 2870 (w), 1508 (vs), 1431 (s), 1354 (s), 1257 (m), 1195 (m), 1076 (m), 945 (m), 725 (m). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): (two series of resonances with ratio about 0.85/1.00) 1.36 (m, 24H, Me), 3.23/3.24 (s, 6H, OMe), 3.95 (m, br, 16H, CH_2), 7.50/7.49 (t, 2H, Ph), 8.50/8.52 (d, 4H, Ph), 9.82/9.90 (s, 2H, Ph).

Data for 8b (R = *i*-Bu). Yield 86% (63.5 mg). Anal. Calcd. for $C_{54}H_{86}N_8O_8Re_2S_4$: C, 43.94; H, 5.87; N, 7.59; S, 8.69%. Found: C, 43.91; H, 5.69; N, 7.64; S, 8.58%. IR (KBr, cm^{-1}): 2959 (m), 2931 (m), 2870 (w), 2808 (w), 1519 (vs), 1420 (s), 1354 (s), 1234 (m), 1149 (m), 1099 (m), 941 (m), 729 (m). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) (two series with ratio: 1.00/0.75): 0.90 (t, 12H, Me), 1.06 (t, 12H, Me), 2.11 (m, 2H, CH), 2.46 (m, 2H, CH), 3.22/3.29 (s, 6H, OMe), 3.75 (m, br, 16H, CH_2), 7.42 (m, 2H, Ph), 8.43/8.45 (d, 4H, Ph), 9.87/9.90 (s, 2H, Ph).

{[ReO{phth(R_2tu)$_2$}]$_4O_2$} (9) and {[ReO{phth(R_2tu)$_2$}]$_2$O}$_n$ (9^n). Freshly prepared compound **8** (0.02 mmol) was dissolved in CH_2Cl_2 (1 mL) and 1 mL of MeCN was added. Slow evaporation of the resulting solution gives a mixture of green crystals of **9** and very fine, green powder of **9^n**.

Data for 9a (R = Et). Yield 72% (17.3 mg). Anal. Calcd. for $C_{72}H_{96}N_{16}O_{14}Re_4S_8$: C, 35.87; H, 4.01; N, 9.30; S, 10.64%. Found: C, 35.70; H, 4.11; N, 9.13; S, 10.48%. IR (KBr, cm^{-1}): 2974 (w), 2931 (w), 1508 (s), 1423 (vs), 1353 (s), 1257 (m), 1195 (m), 1134 (m), 1080 (m), 949 (w), 914 (w), 725 (s), 683 (s), 652 (s). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 1.37 (m, 48H, Me), 3.0–4.5 (m, 32H, CH_2), 7.04 (t, 4H, J = 8,1 Hz, Ph), 8.00 (d, 8H, J = 8,1 Hz, Ph), 9.45 (s, 4H, Ph).

Data for 9^{n}a (R = Et). Yield 28% (6.8 mg). Anal. Calcd. for $(C_{36}H_{48}N_8O_7Re_2S_4)_n$: C, 35.87; H, 4.01; N, 9.30; S, 10.64%. Found: C, 35.72; H, 4.19; N, 9.44; S, 10.68%. IR (KBr, cm^{-1}): 2970 (w), 2924 (w), 2850 (w), 1504 (s), 1427 (vs), 1354 (s), 1254 (m), 1195 (m), 1134 (m), 1076 (m), 910 (w), 725 (s), 655 (s).

Data for 9b (R = *i*-Bu). Yield 80%. (22.9 mg). Anal. Calcd. for $C_{104}H_{160}N_{16}O_{14}Re_4S_8$: C, 43.68; H, 5.64; N, 7.84; S, 8.97%. Found: C, 43.72; H, 5.60; N, 7.69; S, 8.77%. IR (KBr, cm^{-1}): 2955 (m), 2866 (w), 1519 (s), 1492 (m), 1419 (vs), 1353 (m), 1234 (w), 1141 (w), 1095 (w), 937 (w), 729 (m), 694 (s), 663 (m).

Data for 9^{n}b (R = *i*-Bu). Yield 20%. (5.7 mg). Anal. Calcd. for $(C_{52}H_{80}N_8O_7Re_2S_4)_n$: C, 43.68; H, 5.64; N, 7.84; S, 8.97%. Found: C, 43.52; H, 5.71; N, 7.69; S, 8.83%. IR (KBr, cm^{-1}): 2953 (m), 2866 (w), 1521 (s), 1492 (m), 1418 (vs), 1353 (m), 1234 (w), 1141 (w), 1095 (w), 935 (w), 729 (m), 690 (s), 661 (m).

X-ray Crystallography. The intensities for the X-ray determinations were collected on a STOE IPDS 2T instrument with Mo K$_\alpha$ radiation (λ = 0.71073 Å). Standard procedures were applied for data reduction and absorption correction. Structure solution and refinement were performed with SHELXS-97 and SHELXL-97.[11] Hydrogen atom positions were calculated for idealized positions and treated with the "riding model" option of SHELXL. More details on data collections and structure calculations are contained in Table 1. Ellipsoid plots of all structures are shown in Supporting Information, Figures S1–S4. Additional information on the structure determinations has been deposited with the Cambridge Crystallographic Data Centre.

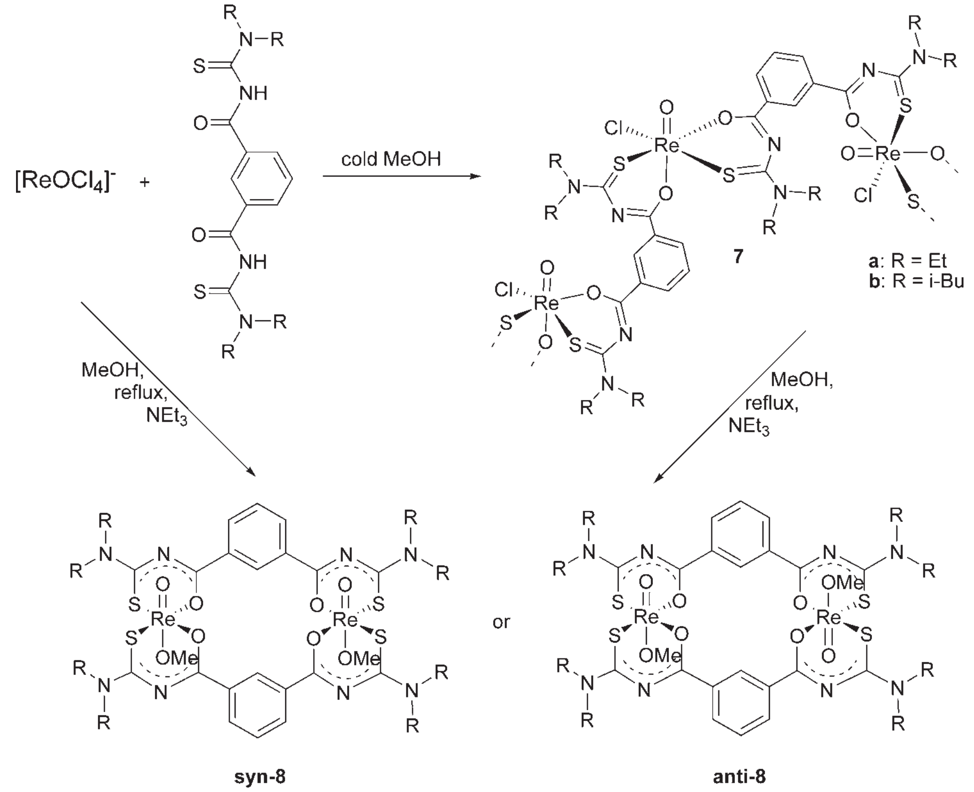
Results and Discussion

Solutions of (NBu_4)[$ReOCl_4$] rapidly react with equivalent amounts of H_2phth(R_2tu)$_2$ in MeOH under immediate formation of almost insoluble green solids of the tentative composition [ReOCl{phth(R_2tu)$_2$}]$_n$ (**7**) (Scheme 1). These intermediate compounds are most probably polymeric complexes with mixed axial/equatorial benzoylthioureato chelating systems (as shown for the monomeric case in the green complexes **4**).[8] The isolation of these compounds from methanol in pure form is complicated, since they slowly undergo a conversion into the red complexes **8**. This color change proceeds much faster in hot MeOH and/or with the addition of a base like Et_3N, and the red product can be isolated almost quantitatively from the final reaction mixture. From cold MeOH, however, the intermediate green solids **7** can be isolated in fair purity, which allows the determination of elemental analyses and IR data. The obtained data, particularly the IR bands of the Re═O bonds which appear at 980 cm^{-1} (**7a**) and 984 cm^{-1} (**7b**) support the supposed composition. These bands appear in the same range as those in complexes **4** and at markedly higher wave numbers than in compounds with alkoxido coligands (compounds **5** and **8**).[8] More spectroscopic studies, particularly NMR spectra were not possible because of the low solubility of the green polymeric complexes. The measurement of mass spectra was only possible in methanol, and they consequently show the appearance of peaks with methoxido coordination. Nevertheless, such mass spectra (e.g., ESI+ of [ReOCl{phth(Et_2tu)$_2$}]$_n$ (**7a**) with peaks at m/z = 595 (5% base peak, [ReOL]$^+$), 1221 (30% base peak,

---

[11] Sheldrick, G. M. *SHELXS-97 and SHELXL-97, Programs for the solution and refinement of crystal structures*; University of Göttingen: Göttingen, Germany, 1997.

Scheme 1. Reactions of $H_2phth(R_2tu)_2$ with $(NBu_4)[ReOCl_4]$



$[(ReO)_2L_2(OMe)]^+$), 1845 (5% base peak, $[(ReO)_3L_3(OMe)_2]^+$) and 2471 (5% base peak, $[(ReO)_4L_4(OMe)_3]^+$) confirm the oligomeric or polymeric nature of **7** by the observation of fragments with three and four rhenium atoms and help to understand the cleavage of the polymers by methanol, as is also observed in the reaction mixture and finally yields to the formation of the dimeric, methoxido-coordinated compounds.[8]

Infrared spectra of complexes **8** exhibit strong bands in the 1500 cm^{-1} region, but no absorptions in the range between 1680 and 1690 cm^{-1}, where the $\nu_{C=O}$ stretches typically appear in the spectra of the non-coordinated $H_2phth(R_2tu)_2$. This corresponds to a bathochromic shift of about 200 cm^{-1} and clearly indicates chelate formation with a large degree of electron delocalization within the chelate rings as has been observed for other rhenium benzoylthioureato complexes.[7] The absence of NH absorption bands in the region of 3100 cm^{-1} indicates the expected deprotonation of the ligands during complex formation. The absorption bands of the Re=O vibration are observed in the range between 940 cm^{-1} and 945 cm^{-1}, which is in the same region of those in the methoxido complex **5**.[8]

Good quality single crystals of **8** are obtained by slow evaporation of their CH_2Cl_2/MeOH solutions. Molecular structures of the products were studied by single crystal X-ray diffraction. Figure 1 depicts the molecular structures of *syn*-**8a** and *anti*-**8b**. Selected bond lengths are compared in Table 2. Both compounds exhibit binuclear structures containing two $\{phth(R_2tu)_2\}^{2-}$ ligands, in which each organic ligand forms two aroylthiourea chelates with two oxorhenium(V) cores in the equatorial plane. The octahedral environments of the rhenium atoms are completed each by a methoxido ligand, which is placed in axial position. Thus, the coordination fashion of each rhenium atom is similar to that reported for **5**.

The two coordination sites in complexes **8a** and **8b** are symmetry related. However, while the symmetry element in **8a** is a glide with the transformation element $(-x, y, 1.5 - z)$, the rhenium atoms in **8b** are related by inversion symmetry $(2 - x, 1 - y, 1 - z)$. These two different symmetry elements consequently result in different orientation of the axial coordination units within the dimeric units. Thus, compound **8a** has two methoxido ligands at the same side of the equatorial plane and represents a *syn* isomer; while in **8b,** the methoxido ligands point to opposite directions and finally form the *anti* isomer of the complex. The bond lengths and angles in the chelate rings are within expected ranges for benzoylthioureato complexes of rhenium.[8] The C−N bond lengths including C2−N6 are significantly shorter than the average length of a C−N single bond,[12] reflecting some degree of double bond character. The Re−O10 bond lengths of 1.711(6) Å in ***syn*-8a** and 1.699(6) Å in ***anti*-8b** are in the typical range of rhenium oxygen double bonds.[13] The Re−O20 bond distances fall in the range between 1.880(**5**) Å and 1.886(**6**) Å and are significantly shorter than expected for a Re−O single bond,[13] but in the same range of Re−OR bonds in several examples of rhenium(V) oxo/alkoxido complexes which have been studied structurally before.[14] This is remarkable with respect to the terminal oxo ligands in the *trans* positions, which should exert a considerable *trans* influence and, thus, weaken these bonds instead of strengthen

---

(12) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans.* **1987**, *2*, S1.

(13) Abram, U. Rhenium. In *Comprehensive Coordination Chemistry II*; McCleverty, J. A., Mayer, T. J., Eds.; Elsevier: Amsterdam, The Netherlands, 2003; Vol. *5*, p 271.

(14) Abram, S.; Abram, U.; Schulz Lang, E.; Strähle, J. *Acta Crystallogr.* **1995**, *C51*, 1078, and references cited therein.

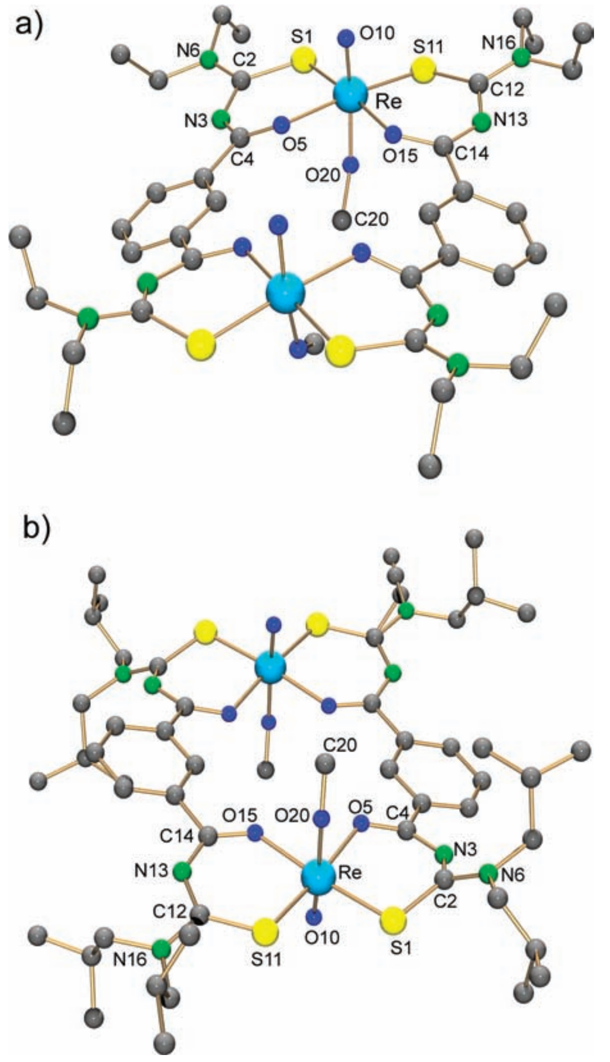


Figure 1. Molecular structure of [ReO(OMe){phth(Et_2tu)$_2$}]$_2$ (*syn*-**8a**) and [ReO(OMe){phth(i-Bu_2tu)$_2$}]$_2$ (*anti*-**8b**). Hydrogen atoms were omitted for clarity.

Table 2. Selected Bond Lengths in *syn*-**8a** and *anti*-**8b**

	syn-**8a**	*anti*-**8b**		*syn*-**8a**	*anti*-**8b**
Re−O10	1.711(6)	1.699(6)	C2−N6	1.332(9)	1.333(9)
Re−O20	1.880(5)	1.886(6)	N3−C4	1.322(9)	1.313(8)
Re−S1	2.323(2)	2.342(2)	C4−O5	1.273(8)	1.266(8)
Re−S11	2.322(2)	2.336(2)	S11−C12	1.765(8)	1.739(8)
Re−O5	2.134(5)	2.109(5)	C12−N16	1.322(9)	1.358(9)
Re−O15	2.123(5)	2.109(4)	C12−N13	1.344(9)	1.347(9)
S1−C2	1.742(7)	1.745(9)	N13−C14	1.317(9)	1.323(9)
C2−N3	1.360(9)	1.338(9)	C14−O15	1.274(9)	1.259(9)

them. However, the shortening of the Re−OR bond is commonly explained by the transfer of some double bond character from the *trans* Re═O bond.[15]

The methoxido complexes **8** are readily soluble in dimethylsulfoxide (DMSO), dimethylformamide (DMF), and chlorinated solvents such as CH_2Cl_2 or $CHCl_3$, but sparingly soluble in alcohols, acetone, or acetonitrile. In solutions, these complexes are only stable in the presence of at least a small amount of MeOH. When MeOH is not added, the solutions slowly change their color from red to green and give precipitates, which are no longer soluble in organic solvents. The green compounds cannot be reconverted into the red complexes by the addition of MeOH and heating as has been previously demonstrated for a similar reaction pattern between compounds **5** and **6**. Recrystallization of compounds **8** from CH_2Cl_2/MeCN solutions gave mixtures of green crystals of the composition [{ReO{phth(R_2tu)$_2$}}$_2$O]$_2$ (**9**) and suspensions of a very fine green powder (**9^n**). The IR spectra of both products show less intense absorptions of Re═O stretches around 915 cm^{-1} and each one additional strong absorption at the region between 655 cm^{-1} and 585 cm^{-1} which is typical for asymmetric Re−O−Re stretches in oxygen bridging rhenium(V) compounds.[16] As in the case of **5**, it can be supposed that in solution, compounds **8** hydrolyze to hydroxido species with traces of water and then are condensed under formation of the oxygen bridged complexes **9** and the polymeric powder **9^n**. Such a reaction scheme is not unusual for oxorhenium(V) compounds and corresponds to frequently observed conversions within the family of Re(V) oxo cores, where charge compensation is one of the main driving forces (Scheme 2).[13]

Interestingly, the ratio between compounds **9** and **9^n** obtained by recrystallization of **8** from CH_2Cl_2/MeCN solutions depends on the concentration of **8**. Particularly, when starting from highly diluted solutions of **8** and slow crystallization, compounds **9** can be obtained in high percentages. Figure 2 illustrates the skeleton of the molecular structures of **9**. Selected bond lengths of compounds **9a** (R = Et) and **9b** (R = i-Bu) are compared in Table 3. The products reveal tetranuclear structures each containing two dimeric blocks which are connected by oxo bridges.

The formation of compound **9a** from a hydrolytic dimerization of the *syn* isomer **8a** is straightforward and easy to understand. It completely corresponds to the previously reported formation of complex **6** from compound **5**,[8] and follows one of the well-known conversion pathways of oxorhenium(V) cores outlined in Scheme 2. The formation of **9b** from *anti*-**8b**, however, is unexpected, since this isomeric form of the complex should only be suitable to form a chain polymer or oligomer, but not a discrete tetrameric molecule. Nevertheless, recrystallization of the compound *anti*-**8b** from a DMSO solution gives quantitatively single crystals of **9b**. This means, compound **9b** must be formed from the *syn* isomer of **8b**, and strongly suggests that solutions of compounds **8** consist of a mixture of *syn* and *anti* isomers. For the solid state, this could not be confirmed. All crystals of **8b** were absolutely unique with respect to their color and shape, and all our attempts to find one single crystal having different cell dimension and structure failed.

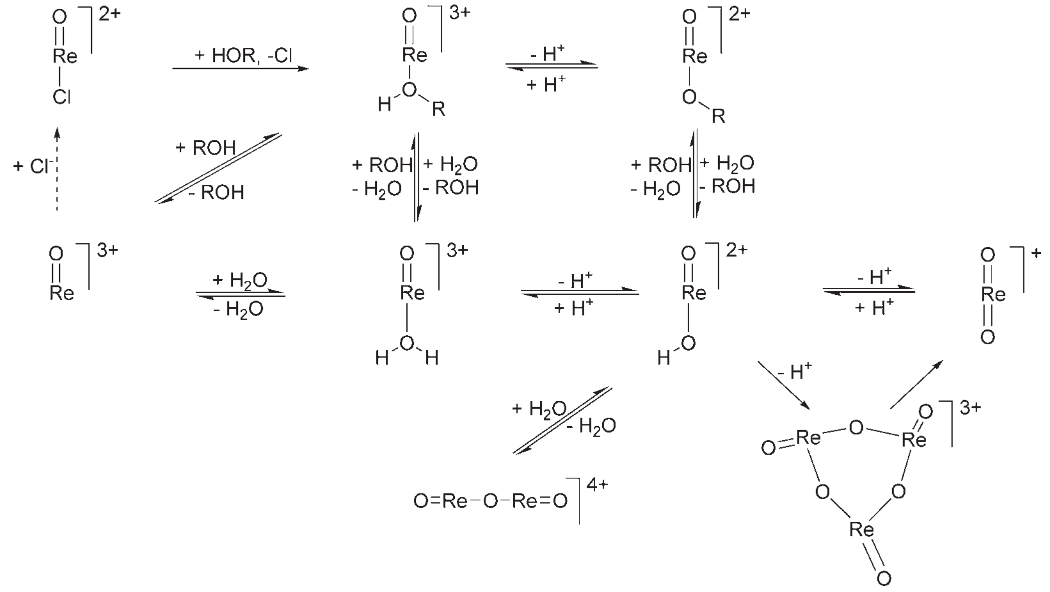
One plausible explanation for the observed formation of compounds **9** from the *syn* as well as from the *anti* isomers of **8** is the presence of both isomers of these complexes in solution. Since a direct isomerization pathway is highly improbable with respect to the rigid chelate framework of the benzoylthioureas, the hydrolysis/methanolysis and protonation/deprotonation equilibria shown in Scheme 3 may play an important role. All reaction steps given there

---

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

(16) (a) Lawrence, A. B.; Paul, E. W.; Grant, N. H. *Inorg. Chim. Acta* **1997**, *255*, 149. (b) Benny, P. D.; Barnes, C. L.; Piekarski, P. M.; Lydon, J. D.; Jurisson, S. S. *Inorg. Chem.* **2003**, *42*, 6519. (c) Gerber., T. I. A.; Tshentu, Z. R.; Garcia-Granda, S.; Mayer, P. *J. Coord. Chem.* **2003**, *56*, 1093.

Scheme 2. Common Oxorhenium(V) Cores and Conversions between Them[13,17]



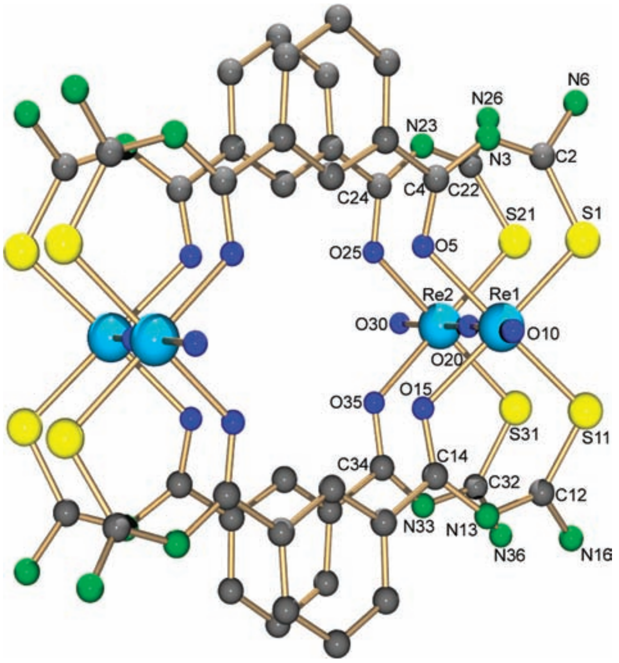


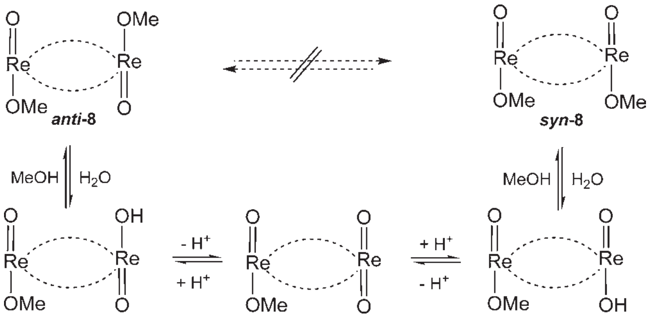
Figure 2. Molecular structure of $[\{ReO\{phth(R_2tu)_2\}\}_2O]_2$ (**9**). Terminal alkyl groups and hydrogen atoms were omitted for clarity.

Table 3. Selected Bond Lengths (Å) in $[\{ReO\{phth(R_2tu)_2\}\}_2O]_2$ (**9**)

	9a	**9b**		**9a**	**9b**
Re1−O10	1.69(1)	1.68(1)	Re2−O30	1.70(1)	1.69(1)
Re1−O20	1.90(1)	1.90(1)	Re2−O20	1.90(1)	1.91(1)
Re1−S1	2.323(4)	2.325(4)	Re2−S21	2.342(4)	2.372(5)
Re1−O15	2.140(9)	2.16(1)	Re2−O35	2.121(9)	2.08(1)
Re1−S11	2.318(4)	2.304(4)	Re2−S31	2.340(4)	2.391(5)
Re1−O5	2.15(1)	2.166(9)	Re2−O25	2.116(9)	2.09(1)

correspond to general conversion patterns between oxorhenium(V) species and have been reported before (Scheme 2). The fact that compound **8a** seems to crystallize preferably as the *syn* isomer while **8b** prefers the *anti* isomer might be explained by the higher lattice energies of the individual compounds, and could be verified by the isolation of compounds with other peripheral substituents. Up to now, however, we were not able to isolate more derivatives of the composition **8** with other residues R.

Scheme 3. Proposed Mechanism for Reversible Transformations between *syn* and *anti* Isomers of **8** in Solution

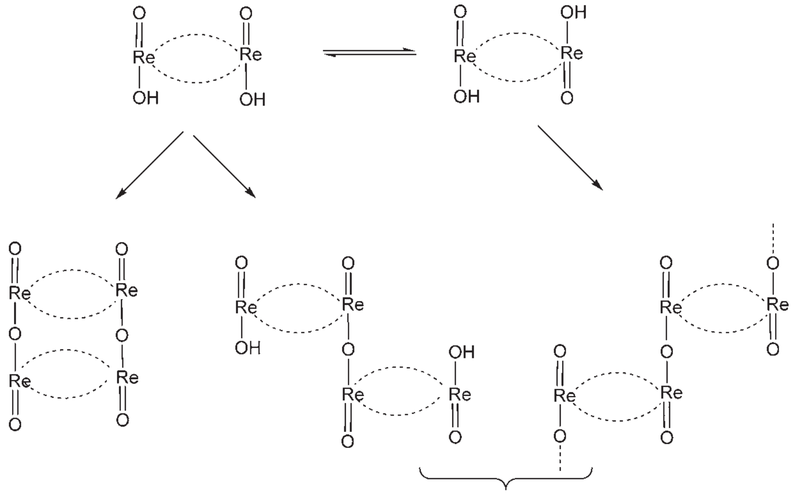


The probable conversion of compounds *syn*-**8** into *anti*-**8** and vice versa via hydrolyzed species (hydroxido complexes and/or oxo-bridged dimers) is supported by the fact that compounds **8** can be kept in $CHCl_3$ solutions without conversion into **9**, when all glassware and solvents were carefully dried prior use. A ^1H NMR study in $CDCl_3$, which was not dried by special procedures, however, confirms a rapid conversion. ^1H NMR spectra of freshly prepared samples of **8** in $CDCl_3$ show two series of signals with the approximate ratios 0.85:1.00 and 1.00:0.75, respectively for **8a** and **8b**, each of which can be attributed to one of the stereo isomers of the binuclear methoxido complexes. Additional signals of low intensities can be assigned to hydrolyzed products. The spectrum is shown in the Supporting Information, Figure S5a. To minimize the hydrolysis of **8** and further condensation, 0.1 mL of MeOH-d_4 was added. Under such conditions, the intensity of the signals, which belong to hydrolyzed products, decreases (Supporting Information, Figure S5b). They completely disappear at a measuring

---

(17) Schroer, J.; Wagner, S.; Abram, U. *Inorg. Chem.* **2010**, *49*, 10694.

Scheme 4. Formation of Tetranuclear Complexes **9** and Oligomeric Compounds **9^n**



9

9^n

(the combination of *anti* and *syn* isomers is possible)

temperature of −70 °C (Supporting Information, Figure S5c) as a consequence of the complete removal of water from the system. This strongly suggests that the hydrolysis and the methanolysis of **8** are in reversible equilibria as is shown in Scheme 3, and the isomerization most probably proceeds via the corresponding hydroxido species.

The discussion above makes plausible that in solution both *anti* and *syn* isomers of the compounds **8** may be present and can convert into each other. During crystallization, however, obviously the isomeric form having the higher lattice energy is preferred. This is the *syn* isomer for **8a** and the *anti* isomer for **8b**. Because of the poor solubility of the formed products, the condensation of the hydroxido species and the formation of the tetrameric and oligomeric oxo-bridged compounds **9** and **9^n** are chemically irreversible. This, and the time which is available for crystallization, may be the main reasons for the different ratios between the crystalline compounds **9** and the fine, polymeric powders **9^n**, which can be obtained and the fact that they vary with the conditions of crystallization (Scheme 4). While a regular molecular composition of **9** is determined by the structures of the binuclear building blocks, oligomerization or polymerization can proceed with a mixture of *syn* and *anti* isomers leading to products with stereochemically less defined composition. This might explain why all our attempts failed to isolate compounds **9^n** in crystalline form.

Conclusions

The coordination chemistry of oxorhenium(V) compounds with 3,3,3′,3′-tetraalkyl-1,1′- isophthaloylbis(thiourea) ligands gives access to binuclear compounds, in which the metal ions are coordinated each by two bidentate O,S moieties of the organic ligands. Two of such compounds can dimerize when the axial methoxido coligand is replaced by hydroxido ligands with subsequent condensation.

The resulting cage type molecule contains a defined empty cavity of an approximate diameter of 5.5 Å, which may be suitable to host large metal ions or small organic molecules. Such host−guest chemistry research is currently underway in our group.

Acknowledgment. H.H.N. gratefully acknowledges grants from the government of Vietnam and the DAAD. We also like to express our thanks to the Center of Supramolecular Interactions (CSI) and the Center International Collaboration (CIC) of Freie Universität Berlin for financial support.

Supporting Information Available: X-ray crystallographic data in CIF format, ellipsoid plots of the crystal structures, and details of an ^{1}H NMR study supporting the presence of *syn* and *anti* isomers of **8** in solution. This material is available free of charge via the Internet at http://pubs.acs.org.