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Article

Rhenium and Technetium Complexes with *N,N*-Dialkyl-*N′*-benzoylthioureas

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N,N-Dialkyl-*N′*-benzoylthioureas, HR^1R^2btu, react under single deprotonation and form air-stable chelate complexes with common rhenium or technetium complexes such as $(NBu_4)[MOCl_4]$ (M = Re, Tc) or $[ReOCl_3(PPh_3)_2]$. Compositions and molecular structures of the products are strongly dependent on the precursors used and the reaction conditions applied. Reactions with $[ReOCl_3(PPh_3)_2]$ in CH_2Cl_2 give complexes of the general formula $[ReOCl_2(R^1R^2btu)(PPh_3)]$ (**3**), with the benzoyl oxygen atom of the chelating benzoylthiourea being trans to the oxo ligand, and/or Re(III) complexes of the composition $[ReCl_2(R^1R^2btu)(PPh_3)_2]$ (**4**) with the PPh$_3$ ligands in trans positions to each other. In polar solvents such as MeOH, EtOH or acetone, corresponding reactions without addition of a supporting base only result in intractable brown solutions, from which no crystalline complexes could be isolated. The addition of NEt$_3$, however, allows the isolation of the bis-chelates $[ReOCl(R^1R^2btu)_2]$ (**1**) in good yields. In this type of complex, one of the chelating $R^1R^2btu^-$ ligands coordinates equatorially, while the second occupies the position trans to the oxo ligand with its oxygen atom. The latter compounds can also be prepared from $(NBu_4)[ReOCl_4]$ in MeOH when no base is added, while the addition of NEt$_3$ results in the formation of $[ReO(OMe)(R^1R^2btu)_2]$ (**5**) complexes with the methoxo ligand trans to O^{2-}. Compounds of the type **5** can alternatively be prepared by heating **1** in MeOH with addition of NEt$_3$. A reversible conversion of **5** into oxo-bridged dimers of the composition $[\{ReO(R^1R^1btu)_2\}_2O]$ (**6**) is observed in water-containing solvents. Starting from $(NBu_4)[TcOCl_4]$, a series of technetium complexes of the type $[TcOCl(R^1R^2btu)_2]$ (**2**) could be prepared. The structures of such compounds are similar to those of the rhenium analogues **1**. Reduction of **2** with PPh$_3$ in CH_2Cl_2 gives Tc(III) complexes of the composition $[TcCl(R^1R^2btu)_2(PPh_3)]$ (**7**) having the chloro and PPh$_3$ ligands in cis positions. When this reaction is performed in the presence of excess chelating ligand, the Tc(III) tris-chelates $[Tc(R^1R^2btu)_3]$ (**8**) are formed.

Introduction

N,N-Dialkyl-*N′*-benzoylthioureas, HR^1R^2btu, are known to form stable complexes with a large number of transition metals.[1] They are versatile ligands with various coordination modes. In the majority of their structurally characterized complexes, they act as bidentate O,S-monoanionic ligands.[2] Coordination as neutral, monodentate S-ligands are found

in some Ag(I) and Au(I) compounds and in a Pt(II) complex,[3] while examples of transition metal complexes with benzoylthioureas as bridging ligands are very rare.[4,5] The structural chemistry of square-planar bis-chelates of benzoylthioureas with d^8 or d^9 ions such as Ni(II), Pd(II), Pt(II), or Cu(II) is dominated by cis isomers,[2c,6] and only a few

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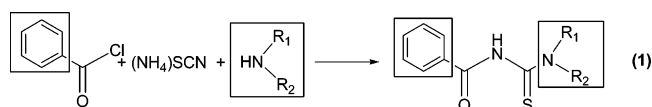
crystal structures of trans-isomers have been elucidated.[7] Photochemical cis/trans isomerization has been studied recently on Pt(II) and Pd(II) complexes, showing that the trans isomers are thermodynamically unstable and readily re-form the cis compounds.[8] Exclusively facial coordination is observed for tris-chelates of benzoylthioureas with Ru(III), Rh(III), and Co(III).[9]

Surprisingly less is known about rhenium and technetium complexes with *N,N*-dialkyl-*N'*-benzoylthioureas. There are only two structurally well characterized rhenium compounds: the neutral oxorhenium(V) complex [ReOCl(Et$_2$-btu)$_2$] (**1c**) and the tricarbonylrhenium(I) compound [Re-(CO)$_3$Br(HEt$_2$btu)$_2$] (**9**).[10,11] The latter one is the only example where chelate formation is observed with a neutral HR$_2$btu ligand. Only one early report describes an synthetic approach to benzoylthioureato complexes of technetium by the reduction of pertechnetate in the presence of the ligands, and the formation of neutral [Tc(R$_2$btu)$_3$] complexes was suggested on the basis of spectroscopic data.[12] This lack of knowledge
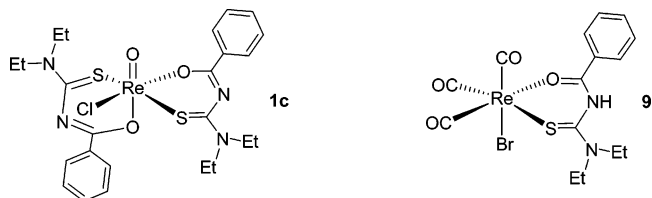
is particularly surprising in light of numerous thiourea complexes of rhenium and technetium, which have been studied extensively and found use as precursors for the synthesis of low-valent Re and Tc complexes.[13]

Our interests in technetium and rhenium complexes with benzoylthioureas mainly are due to the flexibility of this class of ligands, which allows a variety of modifications in the periphery of their chelating system. The compounds are commonly prepared in a one-pot synthesis from benzoyl chloride, (NH$_4$)SCN, and (mainly secondary) amines (eq 1).

This approach allows substitutions at the phenyl ring of the benzoyl unit as well as modifications of the amino site. Particularly the latter one gives access to novel tripodal ligand systems with functionalized amino substituents.

In the present Article, we study some basic reaction patterns of the bidentate chelators with common rhenium and technetium precursors such as [ReOCl$_3$(PPh$_3$)$_2$] or (NBu$_4$)[MOCl$_4$] complexes (M= Re, Tc) including the X-ray structures of the products. Chart 1 illustrates the ligands which were used throughout the experiments.

Experimental Section

Materials. All reagents used in this study were reagent grade and were used without further purification. Solvents were dried and used freshly distilled unless otherwise stated. (NBu$_4$)[MOCl$_4$][13i] and [ReOCl$_3$(PPh$_3$)$_2$][14] were prepared by standard procedures. The synthesis of HR^{1}R^{2}btu ligands was performed by the standard procedure of Beyer et al.[15]

Radiation Precautions. ^{99}Tc is a weak β^--emitter. All manipulations with this isotope were performed in a laboratory approved for the handling of radioactive materials. Normal glassware provides adequate protection against the low-energy β emission of the technetium compounds. Secondary X-rays (bremsstrahlung) play an important role only when larger amounts of ^{99}Tc are used.

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Chart 1. *N*,*N*-Dialkyl-*N*′-benzoylthioureas Used in This Work
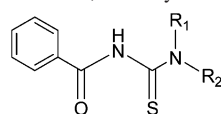
a: HPh₂btu:	R¹ = R² = Ph
b: HPhMebtu:	R¹ = Me, R² = Ph
c: HEt₂btu:	R¹ = R² = Et
d: Hi-Pr₂btu:	R¹ = R² = i-Pr
e: HMorphbtu:	R¹, R² = Morph

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 (results are given in the form: *m/z*, assignment). Elemental analyses of carbon, hydrogen, nitrogen, and sulfur were determined using a Heraeus vario EL elemental analyzer. The technetium analyses were done by liquid scintillation counting. NMR spectra were taken with a JEOL 400 MHz multinuclear spectrometer.

[ReOCl(R¹R²btu)₂] (1), Method 1. HR¹R²btu (0.22 mmol) in 3 mL of acetone was added to a stirred suspension of [ReOCl₃-(PPh₃)₂] (83 mg, 0.1 mmol) in 3 mL of acetone. Three drops of Et₃N were added, and stirring was continued for 30 min at room temperature, whereupon the precursor complex completely dissolved and the color of the reaction mixture changed from yellow-green to deep green. After the mixture was cooled to 0 °C, a colorless precipitate of Et₃N·HCl was filtered off, and the solvent was removed under reduced pressure. Released PPh₃, excess ligand, and small amounts of other, unidentified compounds were removed by washing the resulting residue with 2 mL of cold acetone, and the product remained as an analytically pure, green powder. The separation of the complex can alternatively be done by column chromatography. For this, the crude reaction mixture is loaded onto a silica gel column. The first, yellow fraction of triphenylphosphine and unidentified compounds is eluted with *n*-hexane/acetone (1/1), while the second green fraction containing the complex is eluted with acetone.

Method 2. A solution of (NBu₄)[ReOCl₄] (58 mg, 0.1 mmol) in MeOH (2 mL) was added dropwise while stirring to a solution of 0.22 mmol of the ligand dissolved in 3 mL of MeOH. The color of the solution immediately turned to deep green, and a green precipitate deposited within 30 min. The green powder was filtered off, washed with cold methanol, and recrystallized from CH₂Cl₂/acetone.

Data for 1a (R¹ = R² = Ph). Yield: 45% (41 mg) for method 1; 78% (70 mg) for method 2. Anal. Calcd for C₄₀H₃₀ClN₄O₃S₂-Re: C, 53.35; H, 3.33; N, 6.22; S, 7.11%. Found: C, 53.01; H, 3.10; N, 6.14; S, 7.01%. IR (cm^{-1}): 3040(w), 1485(vs), 1450(vs), 1427(vs), 1380(vs), 1261(m), 1172(m), 1107(w), 1072(w), 975(s), 871(w), 798(w), 756(m), 698(s). ¹H NMR (CDCl₃; δ, ppm): 7.3−8.0 (m, Ph). ¹³C NMR (CDCl₃; δ, ppm): 126−144 (Ph), 174.13 (C=S), 176.04 (C=S), 186.40 (C=O), 194.14 (C=O). FAB$^+$ MS (*m/z*): 865, [M − Cl]$^+$.

Data for 1b (R¹ = Ph, R² = Me). Yield: 44% (34 mg) for method 1; 93% (72 mg) for method 2. Anal. Calcd for C₃₀H₂₆-ClN₄O₃S₂Re: C, 46.41; H, 3.36; N, 7.22; S, 8.25%. Found: C, 46.33; H, 2.95; N, 7.21; S, 8.41%. IR (cm^{-1}): 3035(w), 1473(vs), 1423(vs), 1377(vs), 1269(m), 1172(w), 1103(m), 1072(w), 984(s), 898(m), 798(w), 698(s), 547(s). ¹H NMR (CDCl₃; δ, ppm): 3.87, 3.91, 3.94, 3.96, 3.98, 4.02, 4.13 (7 singlets, 6H, CH₃), 7.1−8.5 (m, 20H, Ph). ¹³C NMR (CDCl₃; δ, ppm): 42.24 (CH₃), 42.76 (CH₃), 126−144 (Ph), 173.53 (C=S), 175.40 (C=S), 185.73 (C=O), 194.11 (C=O). FAB$^+$ MS (*m/z*): 741, [M − Cl]$^+$.

Single crystals suitable for X-ray analysis were obtained by slow evaporation of CH₂Cl₂/acetone or CH₂Cl₂/*n*-hexane solutions.

Data for 1c (R¹ = R² = Et). Yield: 30% (21 mg) for method 1; 91% (64 mg) for method 2. Anal. Calcd for C₂₄H₃₀ClN₄O₃S₂-Re: C, 40.70; H, 4.24; N, 7.91; S, 9.04%. Found: C, 40.31; H, 4.19; N, 7.56; S, 8.81%. IR (cm^{-1}): 3055(w), 2977(w), 2931(w), 2870(w), 1496(vs), 1419(vs), 1358(vs), 1250(m), 1173(w), 1141(m), 1072(m), 980(s), 887(w), 825(w), 794(w), 702(s). ¹H NMR (CDCl₃; δ, ppm): 1.27−1.31 (m, 6H, CH₃), 1.39−1.46 (m, 6H, CH₃), 3.78−3.84 (m, 3H, CH₂), 3.93−3.99 (m, 2H, CH₂), 4.17−4.30 (m, 3H, CH₂), 6.92 (t, 2H, *J* = 7.8 Hz, Ph, *m*-H), 7.36−7.45 (m, 6H, Ph), 8.36 (d, 2H, *J* = 7.4 Hz, Ph, *o*-H). ¹³C NMR (CDCl₃; δ, ppm): 13.13, 13.47, 13.59, and 13.67 (CH₃), 46.79, 47.06, 47.56, and 47.84 (CH₂), 127.49, 128.13, 129.44, 131.38, 131.79, 132.98, 134.40, and 134.94 (Ph), 171.63 (C=S), 174.04 (C=S), 183.06 (C=O), 190.80 (C=O).

[TcOCl(R¹R²btu)₂] (2). The technetium complexes were prepared from (NBu₄)[TcOCl₄] by the procedure described above as method 2 for their rhenium analogues.

Data for 2a (R¹ = R² = Ph). Yield: 70% (57 mg). Anal. Calcd for C₄₀H₃₀ClN₄O₃S₂Tc: Tc, 12.18%. Found: 12.0%. IR (cm^{-1}): 3058(w), 1501(s), 1485(vs), 1450(vs), 1429(vs), 1389(vs), 1261(s), 1172(m), 1107(m), 1072(w), 1022(w), 956(s), 871(w), 798(m), 756(m), 698(s). ¹H NMR (CDCl₃; δ, ppm): 8.06−7.09 (m, Ph).

Data for 2b (R¹ = Ph, R² = Me). Yield: 74% (51 mg). Anal. Calcd for C₃₀H₂₆ClN₄O₃S₂Tc: Tc, 14.37%. Found: 14.1%. IR (cm^{-1}): 3050(w), 1473(vs), 1423(vs), 1381(vs), 1269(m), 1174(w), 1107(w), 1072(w), 1022(w), 964(s), 898(m), 795(w), 698(s). ¹H NMR (CDCl₃; δ, ppm): 3.8−4.1 (br, 6H, CH₃), 7.1−8.0 (m, 20H, Ph).

Single crystals suitable for X-ray diffraction were obtained by slow evaporation of CH₂Cl₂/*n*-hexane solutions of the complexes.

[ReOCl₂(PPh₃)(R¹R²btu)] (3) and **[ReCl₂(PPh₃)₂(R¹R²btu)] (4).** Solid [ReOCl₃(PPh₃)₂] (83 mg, 0.1 mmol) was added to a stirred solution of HR¹R¹btu (0.2 mmol) in CH₂Cl₂ (5 mL). The mixture was stirred at room temperature for 15 min. This resulted in a complete dissolution of [ReOCl₃(PPh₃)₂] and the formation of a green solution. The solvent was removed under vacuum, and the residue was redissolved in 3 mL of acetone. The green-yellow solution slowly changed its color to orange-red. It contained a mixture of the complexes **3** and **4**.

In the case of HPh₂btu, large yellow-orange crystals of **3a** and red plates of **4a** (both types of X-ray quality) deposited together from this solution upon standing for 2 days and were separated mechanically.

Nitromethane (3 mL) was used for the crystallization of the *i*-Pr₂btu$^-$ chelates **3d** and **4d**. Large yellow-green plates of **3d** deposited from such solutions upon standing overnight at room temperature, while small red crystals of **4d** were obtained by slow evaporation of the resulting filtrate in a refrigerator.

Yellow-green crystals of **3e** (the morphbtu$^-$ derivative) were isolated by slow evaporation of the acetone solution described above. All attempts to isolate the corresponding compound **4e** from the remaining solution in crystalline form failed, and only oily, impure products could be recovered.

Data for 3a (R¹ = R² = Ph). Yield: 26% (23 mg). Anal. Cald. for C₃₈H₃₀Cl₂N₂O₂PSRe: C, 52.64; H, 3.48; N, 3.23; S, 3.69%. Found: C, 51.70; H, 3.35; N, 3.41; S, 3.82%. IR (cm^{-1}): 3055(w), 1469(vs), 1439(s),1415(s) 1389(vs), 1272(w), 1095(m) 976(s), 748(m), 694(m), 529(m). ¹H NMR (CDCl₃; δ, ppm): 7.3−8.1 (m, Ph). ¹³C NMR (CDCl₃; δ, ppm): 126−137 (Ph), 172.01 (C=S), 191.23 (C=O). FAB$^+$ MS (*m/z*): 948, [M(NBA) − 2Cl]$^+$; 866, [M]$^+$; 831, [M − Cl]$^+$.

Data for 4a (R¹ = R² = Ph). Yield: 41% (46 mg). Anal. Calcd for C₅₆H₄₅Cl₂N₂OP₂SRe: C, 60.42; H, 4.05; N, 2.52; S, 2.88%.

Found: C, 59.13; H, 4.01; N, 2.39; S, 3.04%. IR (cm^{-1}): 3059(m), 1481(s), 1465(s), 1434(vs), 1365(vs), 1261(m), 1091(m), 1026(w), 744(m), 694(vs), 513(vs). FAB$^+$ MS (*m/z*): 850, [M − PPh$_3$]$^+$; 553, [ReLCl]$^+$.

Data for 3d (R^1 = R^2 = *i*-Pr). Yield: 55% (44 mg). Anal. Calcd for C$_{32}$H$_{24}$Cl$_2$N$_2$O$_2$PSRe: C, 48.11; H, 4.26; N, 3.51; S, 4.01%. Found: C, 48.02; H, 4.05; N, 3.36; S, 4.15%. IR (cm^{-1}): 3055(w), 2977(w), 2933(w), 1481(vs), 1435(vs), 1396(s), 1373(vs), 1307(m), 1265(m), 1145(m), 1096(s), 976(s), 752(s), 694(vs), 509(s). ^{1}H NMR (CDCl$_3$; δ, ppm): 1.11−1.39 (m, 12H, Me), 3.64−3.70 (m, 2H, CH), 7.33−7.66 (m, 20H, Ph). ^{13}C NMR (CDCl$_3$; δ, ppm): 19.26, 19.96 (CH$_3$), 67.75, 68.01 (CH), 127−134 (Ph), 170.27 (C=S), 190.43 (C=O). MS (*m/z*): 881, [M(NBA) − 2Cl]$^+$; 764, [M − Cl + H]$^+$; 729, [M − 2Cl + H]$^+$; 466, [ReOL]$^+$.

Data for 4d (R^1 = R^2 = *i*-Pr). Yield: 18% (19 mg) Anal. Calcd for C$_{50}$H$_{49}$Cl$_2$N$_2$OP$_2$SRe: C, 57.46; H, 4.69; N, 2.68; S, 3.06%. Found: C, 57.03; H, 4.31; N, 2.82; S, 3.34%. IR (cm^{-1}): 3055(m), 2970(w), 2927(w), 1477(s), 1458(s), 1434(vs), 1400(s), 1373(s), 1338(s), 1261(m), 1195(w), 1149(m), 1091(m), 1026(w), 744(m), 694(vs), 516(vs). FAB$^+$ MS (*m/z*): 1044, [M]$^+$; 1009, [M − Cl]$^+$; 782, [M − PPh$_3$]$^+$; 747, [M − Cl − PPh$_3$]$^+$; 712, [ReL(PPh$_3$)]$^+$; 450, [ReL]$^+$.

Data for 3e (R^{1}R^2 = Morph). Yield: 54% (42 mg). Anal. Calcd for C$_{30}$H$_{28}$Cl$_2$N$_2$O$_3$PSRe: C, 45.91; H, 3.57; N, 3.57; S, 4.08%. Found: C, 46.00; H, 3.45; N, 3.47; S, 4.12%. IR (cm^{-1}): 3055(w), 2923(w), 2862(w), 1481(vs), 972(s), 748(m), 694(s), 528(s). ^{1}H NMR (CDCl$_3$; δ, ppm): 7.1−7.8 (m, 20H, Ph), 3.9−4.9 (m, 8H, CH$_2$). ^{13}C NMR (CDCl$_3$; δ, ppm): 49.68, 51.41, 67.00, 67.48 (CH$_2$), 127−135 (Ph), 172.67 (C=S), 190.66 (C=O). FAB$^+$ MS (*m/z*): 866, [M(NBA) − 2Cl]$^+$; 784, [M]$^+$; 749, [M − Cl]$^+$; 714, [M − 2Cl]$^+$.

[ReO(OMe)(Et$_2$btu)$_2$] 5c, Method 1. HEt$_2$btu (52 mg, 0.22 mmol) dissolved in 3 mL of MeOH was added to a solution of (NBu$_4$)[ReOCl$_4$] (58 mg, 0.1 mmol) in MeOH (2 mL). The color of the solution immediately turned to deep green. After the addition of three drops of Et$_3$N and heating, the color of the reaction mixture turned to red and a purple precipitate began to deposit. The mixture was refluxed for 30 min then cooled to 0 °C. The product was filtered off, washed with cold MeOH, and recrystallized from CH$_2$Cl$_2$/MeOH. **5c** can also be synthesized from [ReOCl$_3$(PPh$_3$)$_2$] applying the same reaction conditions.

Method 2. 1c (71 mg, 0.1 mmol) was suspended in 3 mL of MeOH, and three drops of Et$_3$N were added. The mixture was heated on reflux for 15 min, whereupon its color changed from green to red. After the mixture was cooled to 0 °C, a purple precipitate of **5c** was filtered off, washed with MeOH, and dried under vacuum. Yield: 84% (59 mg) for method 1; 90% (63 mg) for method 2. Anal. Calcd for C$_{25}$H$_{33}$N$_4$O$_4$S$_2$Re: C, 42.70; H, 4.69; N, 7.96; S, 9.10%. Found: C, 42.67; H, 4.68; N, 8.03; S, 9.23%. IR (cm^{-1}): 3053(w), 2977(m), 2931(m), 2808(m), 1512(vs), 1500(vs), 1419(vs), 1350(s), 1305(m), 1249(m), 1203(m), 1172(m), 1138(m), 1091(s), 941(s), 887(m), 713(s), 671(m), 493(m). ^{1}H NMR (CDCl$_3$; δ, ppm): 1.34 (t, J = 7.2 Hz, 6H, CH$_3$), 1.28 (t, J = 7.2 Hz, 6H, CH$_3$), 3.17 (s, 3H, OCH$_3$), 3.79−4.01(m, 8 H, CH$_2$), 7.40−746 (m, 6H, Ph, *m*-H and *p*-H), 8.41(d, J = 6.5 Hz, 4H, Ph, *o*-H). ^{13}C NMR (CDCl$_3$; δ, ppm): 12.96, 13.19 (CH$_3$), 46.38, 47.44 (CH$_2$), 57.37(OCH$_3$), 127.98, 130.23, 131.96, and 136.96 (Ph), 172.65(C=S), 180.32(C=O). FAB$^+$ MS (*m/z*): 674, [M − OMe + H]$^+$; 470, [M − L + H]$^+$; 454, [ReO$_2$L]$^+$; 438, [ReOL]$^+$.

[{ReO(Et$_2$btu)$_2$}$_2$O] 6c. Compound **5e** (35 mg, 0.05 mmol) was dissolved in 5 mL of hot MeCN. The mixture was refluxed for 5 min and then slowly cooled to 0 °C. The product precipitated as small green microcrystals. Single crystals of X-ray quality were obtained by slow evaporation of a solution of **6c** in CH$_2$Cl$_2$/MeCN. Yield: 91% (31 mg). Anal. Calcd for C$_{48}$H$_{60}$N$_8$O$_7$S$_4$Re$_2$: C, 42.30; H, 4.41; N, 8.23; S, 9.41%. Found: C, 42.12; H, 4.42; N, 8.30; S, 9.43%. IR (cm^{-1}): 3054(w), 2977(w), 2924(w), 2870(w), 1497(vs), 1423(vs), 1354(s), 1250(m), 1204(m), 1168(w), 1138(m), 1076(w), 953(w), 934(w), 891(m), 725(s), 665(s), 547(w). ^{1}H NMR (CDCl$_3$; δ, ppm): 1.27 (t, J = 7.1 Hz, 6H, CH$_3$), 1.28 (t, J = 7.1 Hz, 6H, CH$_3$), 3.13 (q, J = 6.8 Hz, 2H, CH$_2$), 3.73−3.81 (m, 6H, CH$_2$), 7.33 (t, J = 7.5 Hz, 4H, Ph, *m*-H), 7.42 (t, J = 7.3 Hz, 2H, Ph, *p*-H), 8.25 (d, J = 7.4 Hz, 4H, Ph, *o*-H). ^{13}C NMR (CDCl$_3$; δ, ppm): 13.20, 13.36 (CH$_3$), 45.74, 47.25 (CH$_2$), 127.47, 130.65, 131.33, and 138.10 (Ph), 172.16 (C=S), 182.12 (C=O). FAB$^+$ MS (*m/z*): 1363, [M + H]$^+$; 690, [ReO$_2$L$_2$ + H]$^+$; 673, [ReOL$_2$]$^+$; 454, [ReO$_2$L]$^+$.

[TcCl(PPh$_3$)(Ph$_2$btu)$_2$] 7a. Compound **2a** (40 mg, 0.05 mmol) was dissolved in 5 mL of CH$_2$Cl$_2$, and PPh$_3$ (26 mg, 0.1 mmol) was added. The solution was stirred at room temperature for 3 h. During this time, the color of the solution changed from yellow-brown to deep red. The volume of the solvent was reduced to 2 mL, and 1 mL of MeOH was added. This final solution was slowly evaporated at room temperature resulting in big red crystals of **7a**, which were suitable for X-ray diffraction. Yield: 64% (35 mg). IR (cm^{-1}): 3055(w), 1488(vs), 1435(vs), 1384(vs), 1311(vs), 1176(s), 1118(m), 1011(w), 748(m), 693(s).

[Tc(Ph$_2$btu)$_3$] 8a. HPh$_2$btu (33 mg, 0.1 mmol) and PPh$_3$ (26 mg, 0.1 mmol) were added to a solution of **2a** (40 mg, 0.05 mmol) in 5 mL of CHCl$_3$, and the mixture was stirred at room temperature for 3 h. The color changed from yellow to deep red, and an almost black solid was obtained after removal of the solvent in vacuum. The residue was redissolved in a CH$_2$Cl$_2$/MeOH mixture (1/1), and dark red crystals were deposited after slow evaporation of the solvent. Yield: 75% (42 mg). Anal. Calcd for C$_{61}$H$_{49}$N$_6$O$_4$S$_3$Tc: Tc, 8.80%. Found: 7.8%. IR (cm^{-1}): 3050(w), 1479(vs), 1419(vs), 1366(vs), 1257(s), 1172(w), 1111(w), 1072(w), 1026(w), 756(m), 698(s).

X-ray Crystallography. The intensities for the X-ray structure determinations were collected on a STOE IPDS 2T instrument with Mo Kα radiation (λ = 0.710 73 Å). Standard procedures were applied for data reduction and absorption correction. Structure solution and refinement were performed with SHELXS97 and SHELXL97.[16] Hydrogen atom positions were calculated for idealized positions. More details on data collections and structure calculations are contained in Table 1.

Additional information on the structure determinations have been deposited with the Cambridge Crystallographic Data Centre.
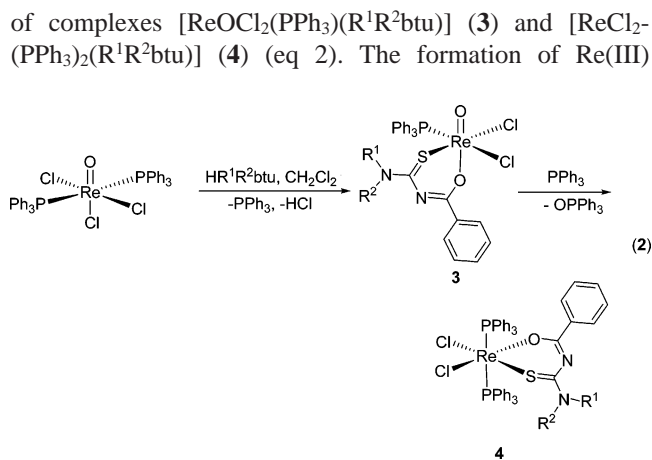
Results and Discussion

Reactions between *N,N*-dialkyl-*N′*-benzoylthiourea ligands, HR^{1}R^{2}btu, and the common rhenium(V) starting material [ReOCl$_3$(PPh$_3$)$_2$] proceed in different ways depending on the solvents and the reaction conditions applied. In the absence of a supporting base, [ReOCl$_3$(PPh$_3$)$_2$] reacts with HR^{1}R^{2}btu in MeOH and EtOH to form unattractive dark brown solids. This result is in accordance with the findings of Dilworth et al.,[10] who were not able to isolate crystalline rhenium complexes with HEt$_2$btu when they started form this precursor. In CH$_2$Cl$_2$ solutions of dialkylbenzoylthioureas, however, the sparingly soluble [ReOCl$_3$(PPh$_3$)$_2$] readily dissolves and yellow-green solutions are formed, which contain mixtures

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

	[ReOCl(PhMebtu)$_2$] **1b**	[TcOCl(Ph$_2$btu)$_2$] **2a**	[ReOCl$_2$(PPh$_3$)- (morphbtu)] **3e**	[ReCl$_2$(PPh$_3$)$_2$- (Ph$_2$btu)] **4a**	[ReO(OMe)- (Et$_2$btu)$_2$] **5c**	[{ReO(Et$_2$btu)$_2$}$_2$O] **6c**	[TcCl(PPh$_3$)(Ph$_2$btu)$_2$]· MeOH **7a**	[Tc(Ph$_2$btu)$_3$]· MeOH **8a**
formula	C$_{30}$H$_{26}$ClN$_4$O$_3$S$_2$Re	C$_{40}$H$_{30}$ClN$_4$O$_3$S$_2$Tc	C$_{30}$H$_{28}$Cl$_2$N$_2$O$_3$PSRe	C$_{56}$H$_{45}$Cl$_2$N$_2$OP$_2$SRe	C$_{25}$H$_{33}$N$_4$O$_4$S$_2$Re	C$_{48}$H$_{66}$N$_8$O$_7$S$_4$Re$_2$	C$_{59}$H$_{49}$ClN$_4$O$_3$PS$_2$Tc	C$_{61}$H$_{49}$N$_6$O$_4$S$_3$Tc
M_w	776.32	812.25	784.47	1113.04	703.90	1361.68	1090.56	1124.24
cryst syst	monoclinic	triclinic	monoclinic	triclinic	monoclinic	monoclinic	triclinic	triclinic
a/Å	19.727(1)	10.763(1)	11.730(1)	12.689(1)	31.573(2)	20.955(9)	12.729(5)	12.999(1)
b/Å	18.811(1)	11.207(1)	19.891(1)	13.114(1)	11.338(1)	15.933(9)	13.286(5)	13.635(1)
c/Å	18.511(1)	16.926(1)	16.864(2)	15.004(1)	16.041(1)	16.661(12)	17.181(5)	16.615(1) Å
α/deg	90	92.48(1).	90	77.87(1)	90	90	73.34(1)	93.08(1)
β/deg	117.85(1)	99.99(1).	130.80(1)	85.38(1)	109.85(1)	108.50(5)	80.06(1)	106.80(1).
γ/deg	90	114.80(1).	90	74.618(1)	90	90	89.27(1)	95.57(1).
V/Å^3	6073.7(6)	1809.9(3)	2978.7(5)	2392.3(3)	5400.9(7)	5275(5)	2740(2)	2795.6(4)
space group	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$C2/c$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
Z	8	2	4	2	8	4	2	2
$D_{calc.}$/g cm^{-3}	1.698	1.490	1.749	1.545	1.731	1.715	1.322	1.336
μ/mm^{-1}	4.265	0.632	4.418	2.805	4.693	4.800	0.464	0.422
no. of reflns	36916	33030	21879	25265	23279	56774	34277	24178
no. of independent reflns	16246	9807	8007	12731	5740	14195	9407	11749
no. params	739	460	361	586	344	618	642	698
R1/wR2	0.0489/0.0975	0.0639/0.1104	0.0284/0.0644	0.0353/0.0851	0.0387/0.0730	0.0782/0.1123	0.0695/0.0947	0.0588/0.1335
GOF	0.946	0.929	1.042	0.978	0.950	1.032	0.839	0.888

of complexes [ReOCl$_2$(PPh$_3$)(R^{1}R^{2}btu)] (**3**) and [ReCl$_2$-(PPh$_3$)$_2$(R^{1}R^{2}btu)] (**4**) (eq 2). The formation of Re(III)

(2)

complexes as minor side-products of such reactions is not unexpected and can be explained by the reduction of the Re(V) oxo complexes by the released PPh$_3$, which attacks the oxo ligands under formation of triphenylphosphine oxide. The presence of OPPh$_3$ in the reaction mixture is confirmed by its ^{31}P NMR signal. The mechanism of the reduction was first proposed by Rouschias and Wilkinson for the synthesis of [ReCl$_3$(MeCN)(PPh$_3$)$_2$][17] and more recently confirmed during reactions of [ReOCl$_3$(PPh$_3$)$_2$] with other systems.[18] A dissociative mechanism with a trigonal-bipyramidal transition state is strongly suggested by the conformation of complexes **4** with the PPh$_3$ ligands in trans positions to each other and with respect to the bulky ligands of **3**.

Infrared spectra of complexes **3** and **4** exhibit strong bands between 1400 and 1500 cm^{-1} but no absorptions in the range between 1670 and 1690 cm^{-1}, where the $\nu_{C=O}$ stretches typically appear in the spectra of the noncoordinated benzoylthioureas.[1] This corresponds to a bathochromic shift of more than 200 cm^{-1} and indicates chelate formation with a large degree of electron delocalization within the chelate rings as has been observed for other R^{1}R^{2}btu$^-$ chelates.[2] The absence of bands in the region of 3100 cm^{-1} indicates the expected deprotonation of the ligands during complex formation. Intense bands between 900 and 1000 cm^{-1}, which can be assigned to the Re=O vibrations,[19] confirm the presence of oxo ligands in **3**, while such bands are absent in the spectra of the rhenium(III) complexes **4**.

FAB$^+$ mass spectra of complexes of type **3** show only less intense signals of the molecular ions. They strongly tend to combine with the matrix 4-nitrobenzylalcohol, and thus, ions of the composition [M + NBA − 2Cl]$^+$ represent peaks of high intensity for these types of complexes. Spectra of complexes **4** are more detailed and show peaks of the molecular ions and fragments, which result from subsequent loss of Cl$^-$ and PPh$_3$.

(17) Rouschias, G.; Wilkinson, G. *J. Chem. Soc. A* **1967**, 993.
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(19) Abram, U. Rhenium. In *Comprehensive Coordination Chemistry II*; McCleverty, J. A., Mayer, T. J., Eds.; Elsevier: Amsterdam, The Netherlands, 2003; Vol. 5, p 271.
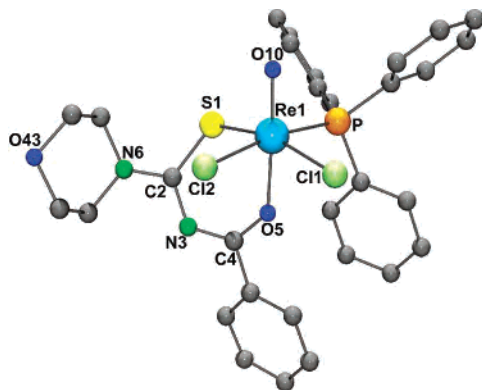
Figure 1. Molecular structure of [ReOCl$_2$(PPh$_3$)(morphbtu)] (**3e**). H atoms have been omitted for clarity.

Table 2. Selected Bond Lengths (Å) in [ReOCl$_2$(PPh$_3$)(morphbtu)] (**3e**) and [ReCl$_2$(PPh$_3$)$_2$(Ph$_2$btu)] (**4a**)

	3e	4a		3e	4a
Re1−O10	1.689(2)		Re1−Cl1	2.379(1)	2.389(1)
Re1−Cl2	2.402(1)	2.385(1)	Re1−S1	2.400(1)	2.360(1)
Re1−O5	2.069(2)	2.021(2)	Re1−P1	2.464(1)	2.486(1)
Re1−P2		2.467(1)	S1−C2	1.761(3)	1.719(4)
C2−N3	1.342(4)	1.341(5)	C2−N6	1.323(4)	1.364(4)
N3−C4	1.315(4)	1.328(4)	C4−O5	1.289(4)	1.270(4)

NMR spectra of complexes **3** provide additional evidence for the proposed composition and molecular structure of the complexes. The spectra are characterized by complex coupling patterns due to hindered rotation around the C−NR^{1}R^2 bonds. This has previously been described for the uncoordinated *N,N*-dialkyl-*N′*-benzoylthioureas and some metal complexes.[6,15,20] A rotational barrier of $\Delta G = 15.5$ kcal/mol was determinded for HEt$_2$btu,[20c] and an increase of this parameter was detected as a consequence of complex formation with Ni(II), Pd(II), or Co(II) ions.[20b] Usually, two sets of signals are observed in ^{1}H and ^{13}C spectra of the Re complexes under study. This may lead to complex coupling patterns in the proton spectra as in that of **3d**, where the CH$_2$ protons show a complex array of overlapping multiplets in the range between 3.9 and 4.9 ppm, and only the ^{13}C NMR spectra clearly show four separated resonances of these CH$_2$ groups at 49.68, 51.41 (CH$_2$N) and 67.00, 67.48 ppm (CH$_2$O). ^{1}H NMR spectra of the paramagnetic Re(III) complexes exhibit broad lines and shall not be the subject of discussion.

Figure 1 depicts the molecular structure of compound **3e** as a prototype for these types of complexes. Selected bond lengths are given in Table 2. The rhenium atom exhibits a distorted octahedral coordination geometry. Axial positions are occupied by an oxo ligand and an oxygen atom of the chelating ligand. The two chloro ligands of the equatorial coordination sphere are in cis arrangement to each other, and the rhenium atom is located 0.221 Å above the mean least-square plane, which is formed from S1, Cl1, Cl2 and P, toward the oxo ligand. The Re=O distance of 1.689(2) Å
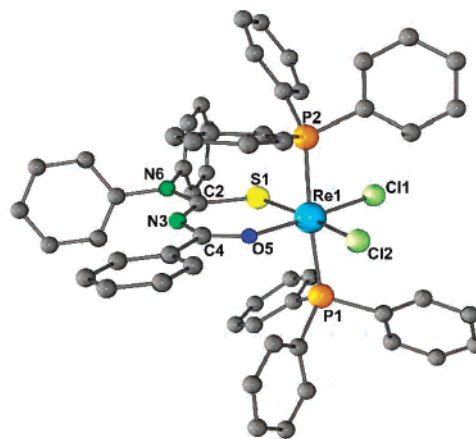

Figure 2. Molecular structure of [ReCl$_2$(PPh$_3$)$_2$(Ph$_2$btu)] (**4a**). H atoms have been omitted for clarity.

is in the expected range of a rhenium−oxygen double bond. A remarkable structural feature is the coordination of the benzoylic oxygen atom trans to the oxo ligand. The Re−O5 bond is expectedly longer than Re−O10 but reflects some double bond character, as has been observed previously for a number of rhenium(V) complexes with oxo and alkoxo ligands in the trans position.[21] Markedly longer Re−OR bonds are found when the alkoxo units are cis to the oxo unit.[22] Despite the fact that the chelate ring is not planar, a considerable extent of π-electron density is indicated by the observed bond lengths. The values of the C−S and C−O bonds are between those expected for carbon−sulfur and carbon−oxygen single and double bonds, and all C−N bonds including the C2−N6 bond are almost equal.

A similar bonding situation is observed in the chelate ring of the rhenium(III) complex **4a**, but in contrast to **3e**, the C2−N6 bond contributes to the conjugated π-system to a lesser extent and the chelate ring is almost planar with a maximum deviation from planarity of 0.04 Å for atom S1. Figure 2 depicts the molecular structure of **4a**, and selected bond lengths are contained in Table 2. The structure reveals a distorted octahedral environment of the rhenium atom with trans coordination of the bulky PPh$_3$ ligands. No unusual bond lengths are observed; the small differences to the structure of **3e** can be addressed by the different oxidation states of the rhenium atoms and/or the influence of the trans ligands.

When acetone is used as the solvent and NEt$_3$ is added as a supporting base, reactions of [ReOCl$_3$(PPh$_3$)$_3$] and an excess of HR^{1}R^{2}btu ligands yield a second ligand exchange product and reduction to Re(III) compounds can be suppressed to a large extent. The different course of the reaction is indicated by a change of the color of the reaction mixture from pale yellow-green to deep green. Green solids can be isolated upon concentration of such solutions, which consist

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Scheme 1
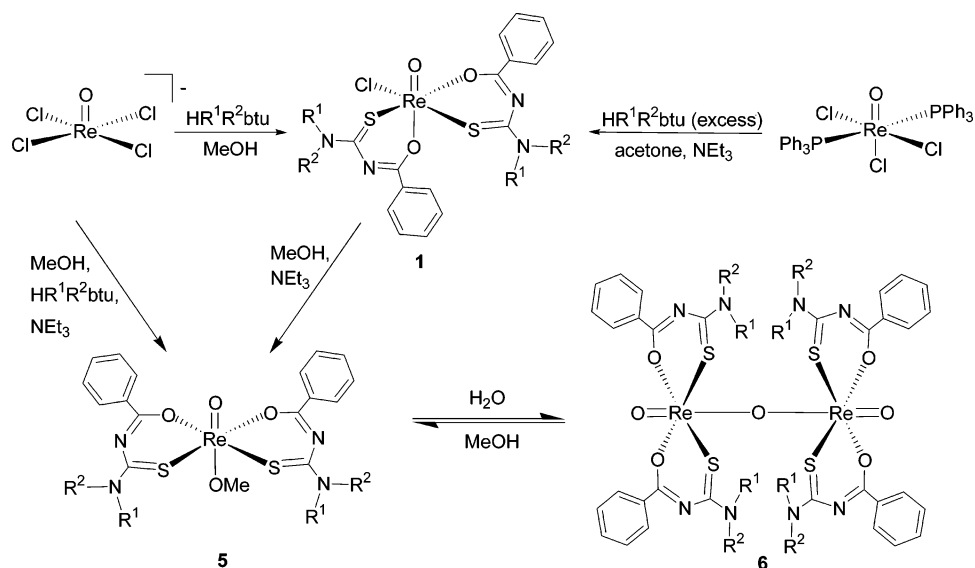
of the bis-chelates [ReOCl(R¹R²btu)₂] (**1**), PPh₃, some traces of **3**, and small amounts of dark unidentified side-products. Purification can be done either by several recrystallizations from acetone or by column chromatography using silica gel. The yields of such reactions can be improved by using a 5-fold excess of the ligands and a prolonged reaction time. A more facile approach to complexes of type **1** is the use of (NBu₄)[ReOCl₄] as a precursor (Scheme 1). Such reactions in methanol give **1** in excellent yields.

IR spectra of **1** show intense bands between 950 and 990 cm⁻¹ which can be assigned to Re=O vibrations. As discussed for complexes of type **3** and **4**, chelate coordination of the R¹R²btu⁻ ligands results in a strong bathochromic shift of the C=O bands, which appear in the spectra in the range between 1400 and 1500 cm⁻¹ and strongly overlap with C=C and C=N bands.

The two sets of resonances of the C=O and C=S carbons atoms in the ¹³C NMR spectra of **1** indicate that the two organic ligands are magnetically inequivalent. The tentative assignment of the C=S and C=O signals has been made under the assumption that complex formation does not result in dramatic changes of their chemical shifts with respect to the positions where these signals appear in the spectra of the uncoordinated benzoylthioureas. The proton NMR spectra are complex due to hindered rotation. In the spectrum of **1b**, which contains the asymmetric PhMebtu⁻ ligands, seven out of eight CH₃ signals, which can be expected due the possible Z,E isomerism of the ligands in such complexes, are resolved. Two of them (3.87 and 3.96) dominate with a relative intensity of approximately 60% and might be assigned to the *E,E* isomer, which is also established in the solid-state structure of the compound (Figure 3). The missing eighth signal of minor intensity is most probably overlapped by one of the others. The ¹³C signals of the less abundant isomers could not be resolved from the noise of the spectrum. Interestingly, the ¹H NMR spectrum of the analogous technetium compound **2b** (vide infra) exhibits only one broad methyl signal, indicating that the rotation barrier of the C–NPhMe bond is lower in the technetium compound.

The molecular structure of **1b** (Figure 3) confirms the results of the spectroscopical studies showing the rhenium atom in a distorted octahedral coordination environment with inequivalent PhMebtu⁻ ligands. One of them binds with its oxygen atom trans to the oxo ligand, similar to the situation in **3**, while the second chelating ligands occupies two equatorial coordination positions. This has significant effects on the bond lengths and angles in the established chelate rings. That of the equatorial ligand is slightly distorted with a maximum deviation from the mean least-square plane of the chelate ring of 0.205 Å for atom Cl2, while the sulfur atom of the axial chelate ring is displaced from a mean least-square plane formed by the atoms Re1, O5, C4, N3, C2, and S2 by 0.367 Å. Selected bond lengths are summarized in Table 3. The distribution of the electrons inside the chelate rings is best described with an extended π-system. The C–N bonds of the ring systems are very similar, and it is evident that considerable π-electron density is transferred to the exocyclic C2–N6 and C12–N16 bonds. This explains the detection of *E/Z* isomers in the ¹H NMR spectrum of the compound.

Addition of a base such as NEt₃ to a refluxing solution of **1c** in MeOH causes an immediate color change from green to red and a complex of the composition [ReO(OMe)(R¹R²-btu)₂] (**5c**) is formed (Scheme 1). Structural analysis of the resulting purple solid reveals that besides the exchange of the chloro by a methoxy ligand, a rearrangement of the chelating ligands is generated. They are both found in equatorial positions in the product with the sulfur atoms cis to each other, while MeO⁻ is found trans to the oxo ligand. Both chelate rings are almost planar in **5c**, the molecular structure of which is shown in Figure 4. The obvious ability of ReO³⁺ cores to transfer electron density to alkoxo ligands in the trans position and the higher degree of delocalized electron density in the equatorial chelate rings seem to be the driving forces of this ligand rearrangement. Several examples of rhenium(V) oxo/alkoxo complexes have been studied structurally before,[21] and in all of these complexes the Re–OR bond is shorter than expected for a Re–O single
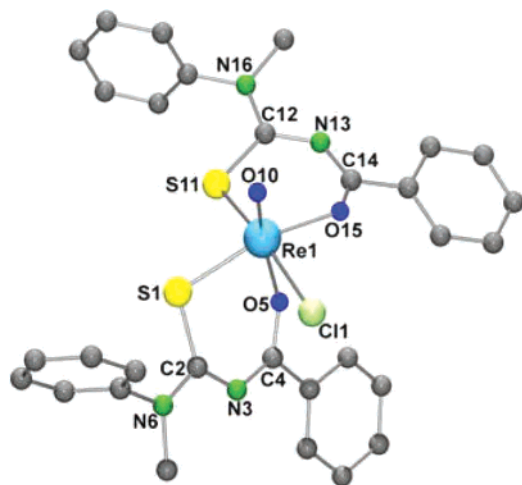
Figure 3. Molecular structure of [ReOCl(PhMebtu)$_2$] (**1b**). H atoms have been omitted for clarity.

Table 3. Selected Bond Lengths (Å) in [ReOCl(PhMebtu)$_2$] (**1b**)^a and [TcOCl(Ph$_2$btu)$_2$] (**2a**)

	1b	**2a**
M1−O10	1.669(6)/1.657(6)	1.642(4)
M1−Cl1	2.432(2)/2.421(2)	2.437(2)
M1−S1	2.343(2)/2.345(2)	2.358(1)
M1−S11	2.319(2)/2.341(2)	2.323(2)
M1−O5	2.098(5)/2.138(5)	2.147(3)
M1−O15	2.052(5)/2.052(5)	2.043(3)
S1−C2	1.760(8)/1.752(8)	1.762(6)
C2−N3	1.33(1)/1.33(1)	1.320(7)
C2−N6	1.33(1)/1.35(1)	1.358(6)
N3−C4	1.33(1)/1.32(1)	1.364(6)
C4−O5	1.287(9)/1.280(9)	1.266(6)
S11−C12	1.765(7)/1.748(8)	1.750(5)
C12−N13	1.36(1)/1.33(1)	1.331(7)
C12−N16	1.31(1)/1.33(1)	1.352(7)
N13−C14	1.31(1)/1.29(1)	1.311(7)
C14−O15	1.28(1)/1.285(9)	1.285(6)

^{a} Two crystallographically independent species.

bond. This is remarkable with respect to the oxo ligands in the trans position, which should exert a considerable trans influence and, thus, weaken these bonds instead of strengthen them.

Nevertheless, the methoxo ligand in **5c** is labile and can readily be replaced by water, which finally yields to the formation of the oxo-bridged dimer [{ReO(Et$_2$btu)$_2$}O] (**6c**). Selected bond lengths of **5c** and **6c** are compared in Table 4. The dimeric complex is formed when **5c** is dissolved in CHCl$_3$ or MeCN and a drop of water is added. This results in an immediate change of the color from red to light green. Signals of **6c** are even observed during ^{1}H NMR measurements on **5c** in CDCl$_3$, when the solvent contains traces of water. On the other hand, the reaction is perfectly reversible and the green solution of **6c** in CHCl$_3$ suddenly turns to red when a small amount of MeOH is added (Scheme 1). A corresponding ^{1}H NMR in the CDCl$_3$ experiment revealed that after the addition of 15 equiv of MeOH, the resonances of **6c** completely disappeared and complex **5c** is exclusively present in such solutions. A dimerization most probably occurs via formation of an intermediate hydroxo species,[23,24] which has not been isolated in the present case. Remarkably, the equilibrium between **5c** and **6c** is completely reversible
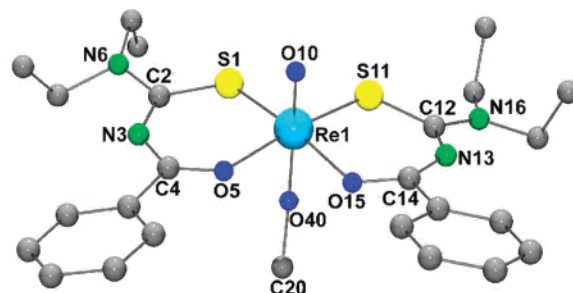

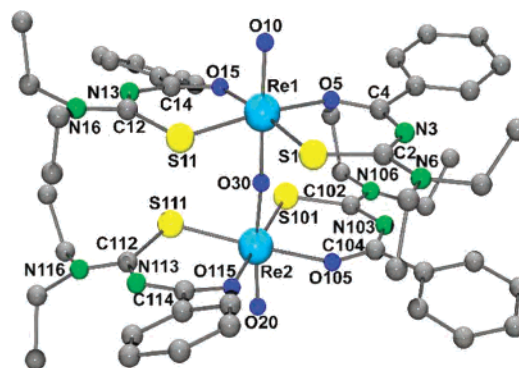**Figure 4.** Molecular structure of [ReO(OMe)(Et$_2$btu)$_2$] (**5c**). H atoms have been omitted for clarity.

Figure 5. Molecular structure of [{ReO(Et$_2$btu)$_2$}$_2$O] (**6c**). H atoms have been omitted for clarity.

Table 4. Selected Bond Lengths (Å) in [ReO(OMe)(Et$_2$btu)$_2$] (**5c**) and [{ReO(Et$_2$btu)$_2$}$_2$O] (**6c**)

	5c	**6c**
Re−O10/O20	1.699(5)	1.703(7)/1.687(8)
Re−S1/S101	2.326(1)	2.340(3)/2.325(3)
Re−S11/S111	2.321(1)	2.334(3)/2.334(3)
Re−O5/O105	2.131(4)	2.089(6)/2.111(7)
Re−O15/O115	2.129(3)	2.101(6)/2.118(7)
Re1−O40	1.795(7)	
Re1−O30 /Re11−O30		1.897(6)/1.914(6)
S1−C2/S101−C102	1.745(6)	1.742(9)/1.74(1)
C2−N3/C102−N103	1.345(7)	1.36(1)/1.35(1)
C2−N6/C102−N106	1.346(7)	1.33(1)/1.33(1)
N3−C4/N103−C104	1.313(7)	1.31(1)/1.30(1)
C4−O5/C104−O105	1.262(6)	1.26(1)/1.27(1)
S11−C12/S111−C112	1.757(5)	1.768(9)/1.74(1)
C12−N13/C112−N113	1.351(7)	1.33(1)/1.33(1)
C12−N16/C112−N116	1.335(6)	1.33(1)/1.34(1)
N13−C14/N113−C114	1.296(7)	1.32(1)/1.32(1)
C14−O15/C114−O1115	1.266(6)	1.27(1)/1.27(1)

under common conditions. In most of the previous examples, the formation of the dimeric species is preferred.[25,26] Only in some exceptional cases, the cleavage of the Re−O−Re backbone of the {Re$_2$O$_3$}$^{4+}$ core has been used to prepare monomeric species, as in the synthesis of [ReO(OEt)Cl$_2$-(py)$_2$] from [Re$_2$O$_3$Cl$_4$(py)$_4$].[24]

The Re=O stretch in the IR spectrum of **6c** is only weak, which is in accord to previous reports,[25] and a strong

(23) Hansen, L.; Alessio, E.; Iwamoto, M.; Marzilli, P. A.; Marzilli, L. G. *Inorg. Chim. Acta* **1995**, *240*, 413.
(24) Johnson, N. P.; Taha F. I. M.; Wilkinson, G. *J. Chem. Soc.* **1964**, 2614.
(25) (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.
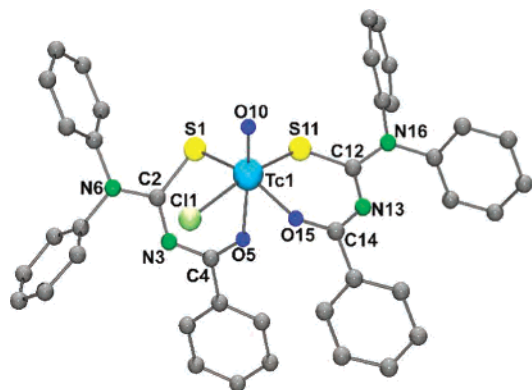
Figure 6. Molecular structure of [TcOCl(Ph$_2$btu)$_2$] (**2a**). H atoms have been omitted for clarity.

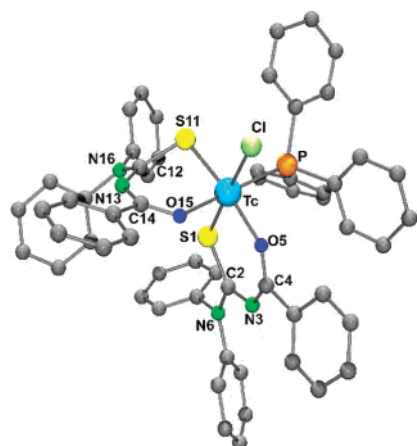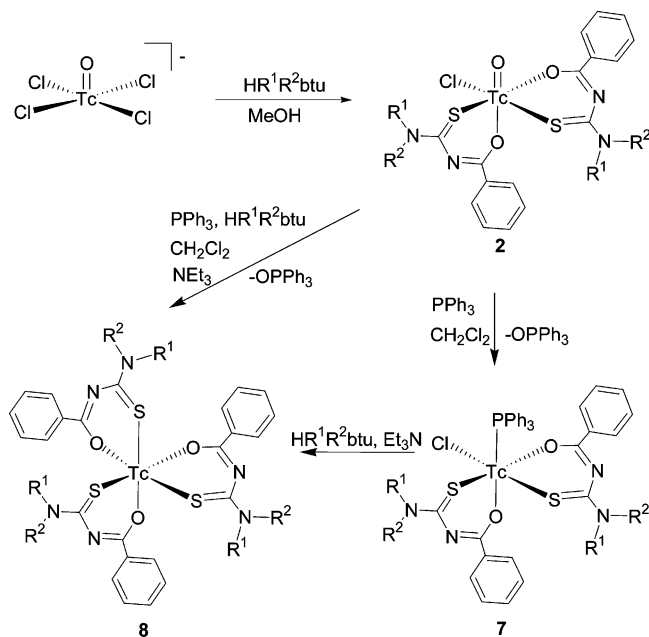**Figure 7.** Molecular structure of [TcCl(PPh$_3$)(Ph$_2$btu)$_2$] (**7a**). H atoms have been omitted for clarity.

Scheme 2

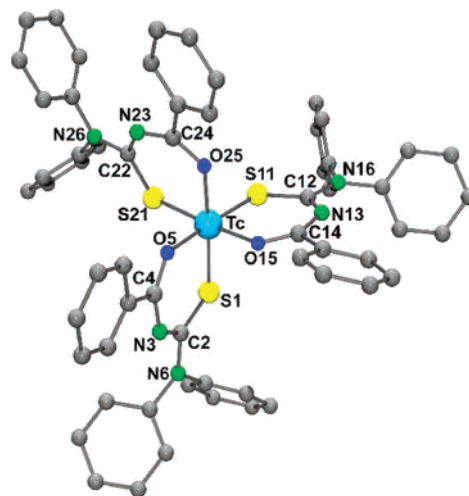**Figure 8.** Molecular structure of [Tc(Ph$_2$btu)$_3$] (**8a**). H atoms have been omitted for clarity.

Table 5. Selected Bond Lengths (Å) in [TcCl(PPh$_3$)(Ph$_2$btu)$_2$] (**7a**) and [Tc(Ph$_2$btu)$_3$] (**8a**)

	7a	8a
Tc−S1/S11/S21	2.333(2)/2.360(2)	2.340(1)/2.352(1)/2.343(2)
Tc−O5/O15/O25	2.044(5)/2.071(5)	2.049(3)/2.046(4)/2.048(4)
Tc−Cl	2.417(2)	
Tc−P	2.428(2)	
S1−C2/S11−C12/S21−C22	1.726(8)/1.723(8)	1.735(6)/1.738(6)/1.738(6)
C2−N3/C12−N13/C22−N23	1.323(9)/1.334(9)	1.329(7)/1.323(7)/1.337(8)
C2−N6 /C12−N16/C22−N26	1.383(7)/1.340(8)	1.370(7)/1.371(6)/1.355(7)
N3−C4/N13−C14/N23−C24	1.346(8)/1.319(9)	1.333(7)/1.327(6)/1.330(7)
C4−O5/C14−O15/C24−O25	1.257(7)/1.280(8)	1.266(6)/1.273(6)/1.278(6)

atoms of the chelate rings. This clearly indicates magnetic equivalence of the Et$_2$btu$^-$ ligands in these two compounds. This is in accord with the structure of **5c** and strongly suggests a similar bonding situation in **6c**.

The spectroscopic results are confirmed by an X-ray structural analysis. Figure 5 illustrates the molecular structure of **6c**, and selected bond lengths are contained in Table 4. The Re−O−Re unit is almost linear (169.9(3)°), and the corresponding bond lengths of 1.897(6) and 1.914(6) Å indicate some double bond character as has been found previously for other compounds with the {Re$_2$O$_3$}$^{4+}$ core.[19] Expectedly (with regard to the NMR results), all chelate rings are almost planar with only negligible deviations (<0.155 Å) are observed.

The structural diversity of the obtained rhenium compounds starting from common precursor complexes encouraged us to undertake similar experiments for technetium. Unfortunately, the analogous PPh$_3$ complex "[TcOCl$_3$-(PPh$_3$)$_2$]" does not exist due to the ready reduction of {TcO}$^{3+}$ centers by monodentate phosphines.[27] Thus, reac-

absorption at 725 cm^{-1}, which is assigned to the asymmetric Re−O−Re stretch, dominates. Two sets of resonances are observed for the ethyl residues in **5c** and **6c** in the ^{1}H and ^{13}C NMR spectra due to the hindered rotation mentioned above, while only one ^{13}C signal is observed for the carbon

(26) (a) Gerber. T. I. A.; Luzipo, D.; Mayer, P. *J. Coord. Chem.* **2005**, *58*, 1505. (b) Kurti, L.; Papagiannopoulou, D.; Papadopoulos, M.; Pirmettis, I.; Raptopoulou, C. P.; Terzis, A.; Chiotellis, E.; Harmata, M.; Kuntz, R. R.; Pandurangi, R. S. *Inorg. Chem.* **2003**, *42*, 2960. (c) Benny, P. D.; Barnes, C. L.; Piekarski, P. M.; Lydon, J. D.; Jurisson, S. S. *Inorg. Chem.* **2003**, *42*, 6519. (d) Tisato, F.; Refosco, F.; Mazzi, U.; Bandoli, G.; Dolmella, A. *Inorg. Chim. Acta* **1989**, *164*, 127. (e) Battistuzzi, G.; Bonamartini-Conradi, A.; Dallari, D.; Saladini, M.; Battistuzzi, R. *Polyhedron* **1999**, *18*, 57.
(27) Alberto, R. Technetium. In *Comprehensive Coordination Chemistry II*; McCleverty, J. A., Mayer, T. J., Eds.; Elsevier: Amsterdam, The Netherlands, 2003; Vol. 5, p 140.

Scheme 3
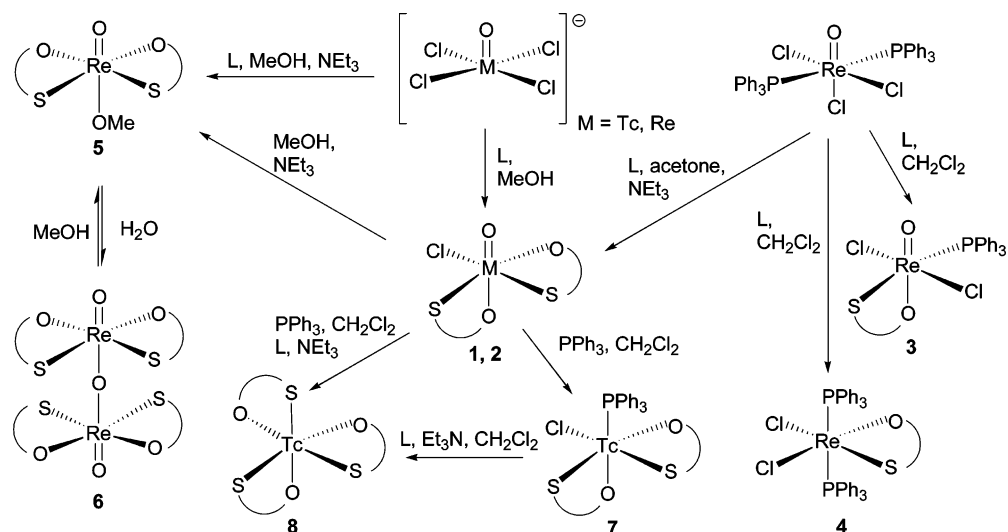
tions of (NBu$_4$)[TcOCl$_4$] with HR^{1}R^{2}btu ligands were studied with methanol as the solvent. They give yellow-brown, crystalline products of the composition [TcOCl(R^{1}R^{2}btu)$_2$] (**2**) in good yields (Scheme 2). The compounds are soluble much better in MeOH than their rhenium analogues **1**, and only small amounts of solvent may be used to obtain the products in good yields.

IR spectra of **2** exhibit the $\nu_{(Tc=O)}$ frequencies in the range between 950 and 970 cm^{-1}, and the spectral features described above for **1**, such as the strong bathochromic shift of the C=O bands, also apply for the Tc compounds. The same holds true for the main structural features of the solid-state structures of the compounds. Figure 6 depicts the molecular structure of **2a**, and the corresponding bond lengths are compared to those of **1b** in Table 2. Again, two chelate rings with different bonding characteristics are observed. An almost planar equatorial chelate ring (maximum deviation from the least-square plan of all atoms of the chelate ring for atom Cl2: 0.201 Å) is accompanied by a strongly distorted ring in the axial position.

The {TcO}$^{3+}$ core is strongly oxidizing, and reactions of **2** with 2 equiv of PPh$_3$ give technetium(III) complexes in good yields even at room temperature. One equivalent of the phosphine is used as a reducing agent, and the formed OPPh$_3$ can readily be detected by ^{31}P NMR in the reaction mixture. The second equivalent is used for coordination in the resulting red [TcCl(PPh$_3$)(R^{1}R^{2}btu)$_2$] complexes (**7**). The products are stable as solids and in solution. Figure 7 shows the molecular structure of **7a**. Selected bond lengths are contained in Table 5. The coordination sphere of the metal is best described as a distorted octahedron with trans angles between 172.9(1) and 177.7(1)°. Triphenylphosphine coordinates trans to the oxygen atom of one of the Ph$_2$btu$^-$ ligands. The chelate ring of this ligand is strongly distorted, while the second one is almost planar. The sulfur atoms are in the cis position to each other.

The chloro and PPh$_3$ ligands in the coordination sphere of **7a** are sufficiently labile to allow further ligand exchange. Thus, the reaction of **7a** with HPh$_2$btu in a CH$_2$Cl$_2$/MeOH mixture yields the dark red-brown tris-chelate [Tc(Ph$_2$btu)$_3$]

(**8a**) in good yields. The same products are formed in a one-pot reaction starting from **2a**, with 2 equiv of PPh$_3$ and an excess of HPh$_2$btu. In both cases, addition of a base such as Et$_3$N supports deprotonation of the *N,N*-dialkyl-*N'*-benzoylthiourea and, thus, the formation of the chelate complex. An alternative synthesis of compounds of the type **8** has been described previously starting directly from pertechnetate with SnCl$_2$ as a reducing agent.[12] This procedure, however, produced a mixture of compounds and a chromatographic purification was necessary, while the present ligand exchange approach gives **8** with high purity and in crystalline form.

Figure 8 illustrates the molecular structure of complex **8a**. It shows only minor deviations from idealized octahedral geometry with trans angles in the range 174.4(1)−176.0(1)°. The distorted octahedral geometry is defined by two sets of three facially bound sulfur and oxygen atoms from three Ph$_2$btu$^-$ ligands. All chelate rings in **8a** are almost planar. The O−Tc−O bond angles fall in the range 84.5(2)−86.3(2)° which is slightly smaller than the S−Tc−S bond angles (90.4(1)−91.1(1)°). Similar patterns have been observed previously for the tris-chelates *fac*-[Ru(Et$_2$btu)$_3$], *fac*-[Rh-(Et$_2$btu)$_3$], *fac*-[Co(Et$_2$btu)$_3$], and *fac*-[Co(Morphbtu)$_3$].[9]

Conclusions

N,N-Dialkyl-*N'*-benzoylthioureas are versatile ligands, which form stable complexes with rhenium and technetium. Irrespective of the oxidation states of the metals and/or the cores, they act as monoanionic chelates (Scheme 3). The bonding situation inside the chelate rings manifests a high degree of delocalization of electron density, which also includes the exocyclic C−N bonds. The composition of the coordination sphere of the metal ions can be controlled by the reaction conditions applied and by coligands such as phosphines or alcoholates.