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Synthesis and Reactivity of Structurally Analogous Phenylimido and Oxo Complexes of Rhenium(V) with N,N-Dialkyl-N′-benzoylthioureas

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Abstract. $[ReOCl_3(PPh_3)_2]$ and $[Re(NPh)Br_3(PPh_3)_2]$ react at room temperature with equivalent amounts of N,N-dialkyl-N′-benzoylthioureas (HR^1R^2btu) in CH_2Cl_2 under formation of the rhenium(V) complexes $[ReOCl_2(R^1R^1btu)(PPh_3)]$ and $[Re(NPh)Br_2(R^1R^2btu)(PPh_3)]$, respectively. The products are structurally analogous with the oxygen atoms of the benzoylthioureas binding in trans positions to the oxo or phenylimido ligands. Prolonged reaction times result in the reduction of the oxo compound by the released PPh_3 and the formation of rhenium(III) complexes of the composition $[ReCl_2(PPh_3)_2(R^1R^2btu)]$, while such a second reaction path is excluded for the phenylimido compound. Phenylimido species with more than one N,N-dialkyl-N′-benzoylthioureato ligand could not be isolated, even when a large excess of HR^1R^2btu was used during the reaction.

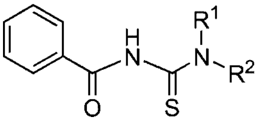
Keywords: Rhenium; Benzoylthioureas; Oxo complexes; Phenylimido complexes; Structure analysis

Introduction

N,N-Dialkylbenzoylthioureas, HR^1R^2btu, are known to form stable complexes with a large number of transition metals [1]. In the majority of their structurally characterized complexes they act as bidentate O,S-monoanionic ligands [2]. Coordination as neutral, monodentate S-ligands can be found in some Ag^I, 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].

We are interested in complexes of technetium and rhenium with benzoylthiourea ligands mainly due to the flexibility of the periphery of their chelating system, which allows the control of the lipophilicity of the complex and gives access to bioconjugated rhenium and technetium compounds. In a previous paper [6], we reported the complicated pattern of reactions of benzoylthioureas with $[ReOCl_3(PPh_3)_2]$, which is a common starting material for the synthesis of rhenium(V) oxo complexes. In CH_2Cl_2, such reactions give two different products: complexes of the general formula $[ReOCl_2(R^1R^2btu)(PPh_3)]$ (**1**), and/or Re^{III} complexes of the composition $[ReCl_2(R^1R^2btu)(PPh_3)_2]$ (**2**). The formation of the Re^{III} compounds is the result of reduction of Re^V by released PPh_3. We have now extended these studies to the phenylimido core.

Here, we report the synthesis and molecular structures of the Re^V phenylimido complexes of the composition $[Re(NPh)Br_2(R^1R^2btu)(PPh_3)]$ together with the structural data of analogous Re^V oxo compound $[ReOCl_2(^iPr_2btu)(PPh_3)]$, and compare the chemical behavior, spectroscopic data and structures of the two classes of benzoylthiourea complexes. Chart 1 illustrates the ligands which were used throughout the experiments.



a) H^iPr_2btu $R^1 = R^2 = {}^iPr$

b) HPh_2btu $R^1 = R^2 = Ph$

c) HMorphbtu R^1, R^2 = Morph

Chart 1 N,N-Dialkylbenzoylthioureas, HR^1R^2btu, used in this work

Results and Discussion

The phenylimido and the oxo cores of rhenium(V) complexes, $[Re{=}NPh]^{3+}$ and $[Re{=}O]^{3+}$, are chemically very similar [7]. This has been demonstrated by the synthesis of a number of structurally analogous complexes, including the triphenylphosphine complexes $[ReOX_3(PPh_3)_2]$ (X = Cl, Br) and $[Re(NPh)X_3(PPh_3)_2]$ (X = Cl, Br, I). They are used as common precursors in the synthesis of other Re^V oxo and Re^V phenylimido complexes by ligand exchange reactions [7, 8]. Reactions of N,N-dialkyl-N′-benzoylthioureas with these two starting materials, however, show a slightly different course of the reactions.

$[ReOCl_3(PPh_3)_2]$ readily reacts with H^iPr_2btu at room temperature in CH_2Cl_2 under formation of the yellow-green main product $[ReOCl_2(^iPr_2btu)(PPh_3)]$ (**1a**) and the deep-red side product $[ReCl_2(^iPr_2btu)(PPh_3)_2]$ (**2a**). Deep-green bis-chelates of the formula $[ReOCl(R^1R^2btu)_2]$ are formed, when such reactions are performed in acetone using two

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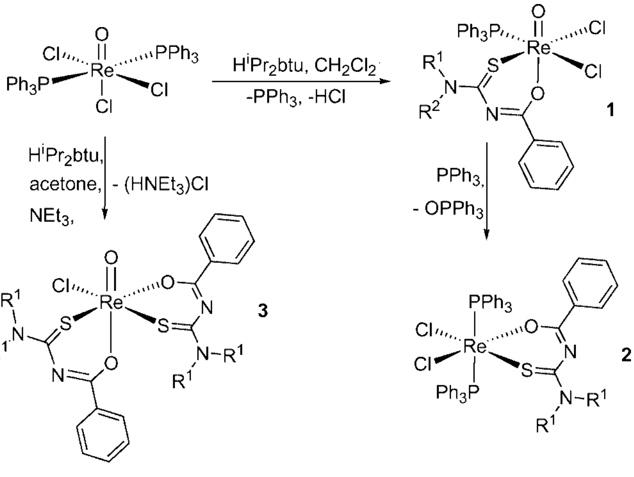
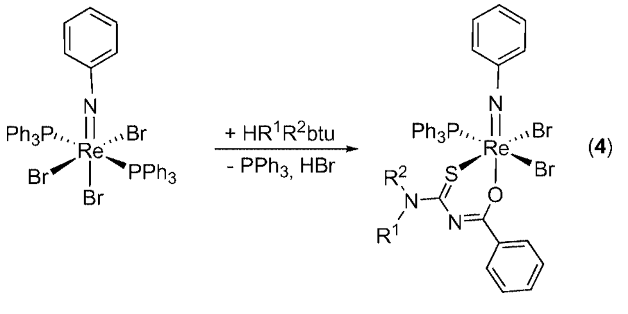
equivalents of the corresponding benzoylthioureas with the addition of NEt_3 as a supporting base (Scheme 1). The spectroscopic data of the products have been published previously together with those of some other representatives of oxorhenium(V) and rhenium(III) complexes with N,N-dialkyl-N′-benzoylthioureas [6].



Scheme 1

In contrast to the behavior of $[ReOCl_3(PPh_3)_2]$, the phenylimido complex $[Re(NPh)Cl_3(PPh_3)_2]$ does not react in CH_2Cl_2 or acetone with benzoylthioureas under ambient conditions. Prolonged heating on reflux in CH_2Cl_2 and the addition of NEt_3 as a supporting base resulted in the gradual consumption of $[Re(NPh)Cl_3(PPh_3)_2]$, but results in the formation of intractable brown solutions. Unfortunately, all our attempts to isolate crystalline product from the reactions of this precursor failed.

More successful were reactions using another Re^V phenylimido precursor, $[Re(NPh)Br_3(PPh_3)_2]$. The bromo derivative is slightly better soluble and quickly reacts with the corresponding benzoylthioureas in warm CH_2Cl_2 under formation of $[Re(NPh)Br_2(Ph_2btu)(PPh_3)]$ (**4b**) and $[Re(NPh)Br_2(Morphbtu)(PPh_3)]$ (**4c**). The yellow-green solids can be isolated in good yields from the yellow-green solutions as the sole products (Scheme 2). No further reduction of the products was found. This comes not completely unexpected, since the formation of rhenium(III) side products during ligand exchange reactions starting from $[ReOCl_3(PPh_3)_2]$ is commonly explained by an attack of released PPh_3 to the oxo ligand with subsequent formation of $OPPh_3$ and reduction of the metal ion. This is certainly not possible with the phenylimido species under study. An additional stabilization of the higher oxidation state might be given by the fact that the nitrogen atom is a stronger π electron donator and a weaker electron acceptor than the oxygen atom as has been discussed recently [9]. Experimental support for this discussion is given by ^{31}P-NMR, which shows the presence of a considerable amount of $OPPh_3$ in the reaction mixture of the oxo compounds, while only the signals of the $[Re(NPh)Br_2(R^1R^2btu)(PPh_3)]$ complexes and released PPh_3 could be detected in the spectra of reaction mixtures of the phenylimido compounds. The use of an excess of HR^1R^2btu during the reactions did not result in the formation of a further ligand exchange products with more than one of the chelating ligand.



Scheme 2

The **infrared spectra** of the imido compounds are very similar to those of the oxo complexes. All exhibit strong bands between 1470 and 1510 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 non-coordinated benzoylthioureas [1]. This corresponds to a strong bathochromic shift of approximately 200 cm^{-1} and indicates chelate formation with a large degree of electron delocalization within the chelate rings [2]. The absence of ν_{NH} bands in the region of 3100 cm^{-1} indicates the expected deprotonation of the ligands during complex formation. The Re=N vibrations can not be assigned unambiguously in the IR spectra of **4b** and **4c**, while an intense band at 976 cm^{-1} can be assigned to the $\nu_{Re=O}$ stretch in the spectrum of **1a**. The FAB^+ mass spectrum of the phenylimido complex **4b** shows an intense signal for the molecular ions at m/z = 1032, while the the spectrum of the oxo compound **1a** is dominated by fragment peaks at m/z = 881 (M(NBA)−2Cl), 764 (M-Cl+H), 729 (M-2Cl+H) and 466 (M-2Cl-PPh_3).

NMR spectra of the compounds **4b** and **4c** 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 $C-NR^1R^2$ bonds. This has previously been described for the uncoordinated N,N-dialkylbenzoylthioureas and some of their metal complexes [10], and leads to complex coupling patterns in the proton spectra as in that of **4c**. The CH_2 protons show a complex array of overlapping multiplets in the range between 3.8 and 4.7 ppm and only the ^{13}C NMR spectra clearly show four separated resonances of these CH_2 groups at 48.79, 51.16 for (CH_2-N) and 66.51, 67.38 ppm for (CH_2O). The signals of the C=O carbon atoms in **4b** and **4c** appear in the region of 190 ppm which well agrees with the corresponding chemical shift detected in the ^{13}C-NMR spectrum of **1a** (190.43 ppm).

The **X ray structure studies** confirm the analogous structures of **1a** and **4b**. Figure 1 and 2 depict the ORTEP diagrams of the molecules. Selected bond lengths and angles are compared in Table 1. The rhenium atoms are found in

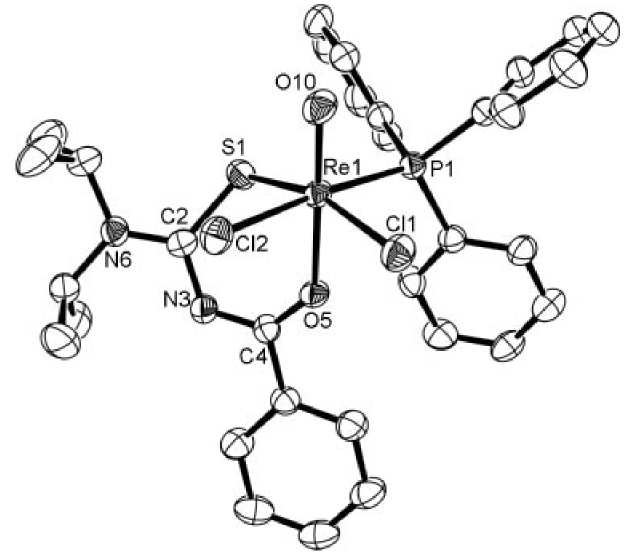


Figure 1 Ellipsoid representation [16] of the molecular structure of $[ReOCl_2(PPh_3)(^iPr_2btu)]$. Hydrogen atoms are omitted for clarity.

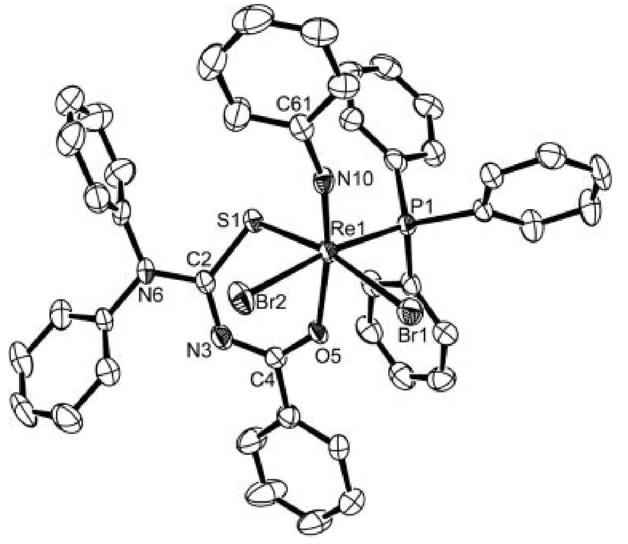


Figure 2 Ellipsoid representation [16] of the molecular structure of $[Re(NPh)Br_2(PPh_3)(Ph_2btu)]$. Hydrogen atoms are omitted for clarity.

Table 1 Selected bond lengths /Å and angles /° in $[ReOCl_2(PPh_3)(^iPr_2btu)]$ (**1a**) $[Re(NPh)Br_2(PPh_3)(Ph_2btu)]$ (**4b**)

	1a	**4b**		**1a**	**4b**
Re1−O10 / N10	1.679(4)	1.725(6)	S1−C2	1.763(6)	1.749(6)
Re1−P1	2.471(1)	2.422(2)	C2−N6	1.325(7)	1.363(8)
Re1−Cl1 / Br1	2.382(1)	2.535(1)	C2−N3	1.351(6)	1.316(9)
Re1−Cl2 / Br2	2.405(1)	2.605(1)	N3−C4	1.313(7)	1.322(9)
Re1−S1	2.392(1)	2.415(2)	C4−O5	1.288(6)	1.283(8)
Re1−O5	2.068(3)	2.064(4)	N10−C61		1.366(9)
O10/N10−Re1−O5	175.8(2)	170.7(2)	O5−Re1−Cl1/Br1	82.1(1)	83.1(1)
O10/N10−Re1−Cl1/Br1	101.7(2)	102.8(2)	O5−Re1−S1	80.1(1)	82.1(1)
O10/N10−Re1−S1	96.2(2)	92.0(2)	O5−Re1−Cl2/Br2	84.5(1)	82.8(1)
O10/N10−Re1−Cl2/Br2	97.6(2)	90.1(2)	O5−Re1−P1	89.1(1)	89.6(1)
O10/N10−Re1−P1	88.7(2)	97.7(2)	Cl1/Br1−Re1−S1	162.2(1)	165.1(1)
Cl1/Br1−Re1−Cl2/Br2	86.7(1)	88.6(1)	S1−Re1−P1	86.9(1)	91.3(1)
Cl1−Re1−P1	93.9(1)	87.7(1)	Cl2/Br2−Re1−P1	173.5(1)	171.9(1)
S1−Re1−Cl2	90.6(1)	90.5(1)	C61−N10− Re1		162.9(4)

distorted octahedral coordination environments in both structures. The axial positions are occupied by the oxygen atoms of the chelating ligands and the double bonded oxygen or nitrogen atoms of the oxo or phenylimido ligands. The equatorial planes are formed by the sulphur atoms of the singly deprotonated benzoylthioureas, the phosphorus atoms and the halogeno ligands, which are in cis arrangement to each other. The rhenium atom is located above the mean least-square plane formed by the equatorial donor atoms by 0.201 and 0.194 Å in **1a** and **4b**, respectively, towards the Re=O and Re=N double bonds. The Re=O bond length in **1a** of 1.679(4) Å is in the expected range of a rhenium−oxygen double bond [7], whereas the Re=N distance of 1.725(6) Å in **4b** is slightly shorter with respect to some other Re^V phenylimido complexes having an oxygen atom coordinated trans to a NPh^{2-} ligand [11]. Despite the fact that the chelate rings are not planar in both compounds (main deviations from the planarity is indicated each for the atoms S1 in both compounds, 0.490(2) Å in **1a** and 0.433(3) Å in **4b**), a considerable delocalization of π-electron density throughout the chelate rings is indicated by the observed bond lengths. The respective values of the C−S and C−O bonds are between those expected for carbon−sulphur and carbon−oxygen single and double bonds. All C−N bond lengths including the C2−N6 bonds are almost equal.

Experimental Section

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. $[ReOCl_3(PPh_3)_2]$ [12] and $[Re(NPh)Cl_3(PPh_3)_2]$ [13] were prepared by standard procedures. The synthesis of benzoylthioureas was performed by the standard procedure of *Beyer* et al. [14].

Table 2 X-ray structure data collection and refinement parameters.

	[ReOCl$_2$(PPh$_3$)(^{i}Pr$_2$btu)]	**[Re(NPh)Br$_2$(PPh$_3$)(Ph$_2$btu)]**
Formula	$C_{32}H_{34}Cl_2N_2O_2PReS$	$C_{44}H_{35}Br_2N_3OPReS$
M$_w$ /g mol^{-1}	798.74	1030.80
Crystal system	monoclinic	monoclinic
a/ Å	9.911(1)	12.208(1)
b/ Å	19.233(1)	19.265(1)
c/ Å	16.768(1)	17.257(1)
β/ °	92.03(1)	93.59(1)
V/ Å^3	3194.3(4)	4050.8(5)
Space group	P2$_1$/n	P2$_1$/c
Z	4	4
D$_{calc.}$/g cm^{-3}	1.661	1.690
μ/ mm^{-1}	4.119	5.101
Absorption correction	Numerical/integration	Numerical/integration
T$_{min}$/T$_{max}$	0.4327/0.6600	0.2927/0.5224
No. of reflections	22445	19089
No. of independent/ R(int)	8558 / 0.0516	8559 / 0.0577
No. parameters	370	478
R1/wR2	0.0440 / 0.1009	0.0522 / 0.1281
GOF	0.913	1.020
Deposit reference number	CCDC 682101	CCDC 682102

Infrared spectra were recorded from KBr pellets on a Shimadzu FT instrument in the range 400−4000 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 were determined using a Heraeus vario EL elemental analyzer. NMR-spectra were taken at 25 °C with a JEOL 400 MHz multinuclear spectrometer. The X-ray diffraction data were collected on a STOE IPDS diffractometer with Mo Kα radiation. The structures were solved by the Patterson method using SHELXS-97 [15]. Subsequent Fourier-difference map analyses yielded the positions of the non-hydrogen atoms. Refinement was performed using SHELXL-97 [15]. The positions of hydrogen atoms were calculated for idealized positions and treated with the 'riding model' option of SHELXL-97. Crystal data and more details of the data collections and refinements are contained in Table 2. Additional information on the structure determinations have been deposited at the Cambridge Crystallographic Data Centre.

[ReOCl$_2$(^{i}Pr$_2$btu)(PPh$_3$)] (1a). The compound was prepared from [ReOCl$_3$(PPh$_3$)$_2$] and H^{i}Pr$_2$btu as described previously [6]. Single crystals suitable for X-ray study were obtained by slow evaporation of a CH$_2$Cl$_2$/MeCN solution.

Elemental analysis: Calcd. for $C_{32}H_{24}Cl_2N_2O_2PSRe$: 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$_3$; ppm): 1.11−1.39 (m, 12H, Me), 3.64−3.70 (m, 2H, CH), 7.33−7.66 (m, 20H, Ph). **^{31}P-NMR** (CDCl$_3$; ppm): −5.23 (s); **^{13}C NMR** (CDCl$_3$; ppm):19.26, 19,96(CH$_3$), 67.75, 68.01 (CH), 127−134(Ph), 170.27(C=S), 190.43(C=O). **FAB$^+$-MS** (m/z): 881 [M(NBA)-2Cl]$^+$, 764 [M-Cl+H]$^+$, 729 [M-2Cl+H]$^+$, 466 [ReOL]$^+$.

[Re(NPh)Br$_2$(PPh$_3$)R^{1}R^{2}btu] (4). Solid HR^{1}R^{2}btu (0.15 mmol) was added to a stirred suspension of [Re(NPh)Br$_3$(PPh$_3$)$_2$] (104 mg, 0.1 mmol) in 5 ml of CH$_2$Cl$_2$. The temperature of the mixture was kept at 30 °C for 1h. During this time, the precursor complex completely dissolved and a clear yellow-green solution was obtained. The solvent was removed under vacuum to dryness and the residue was recrystallized from 3 ml acetone.

4b (R^1 = R^2 = Ph): Yield: 70 % (72 mg). Elemental analysis: Calcd. for $C_{44}H_{35}Br_2N_3OPSRe$: C, 51.25; H, 3.40; N, 4.08; S, 3.11. Found: C, 51.21; H, 3.08; N, 3.78; S, 3.08 %.

IR (KBr, cm^{-1}): 3055(w), 1481(s), 1431(vs), 1400(vs), 1257(w), 1173(w), 1091(m), 1072(w), 1026(m), 999(w), 759(m), 694(s), 528(s). **^{1}H-NMR** (CDCl$_3$; ppm): 7.0−7.5 (m, 35H, Ph). **^{31}P-NMR** (CDCl$_3$; ppm): 1.06 (s); **^{13}C-NMR** (CDCl$_3$; ppm): 121−134 (Ph), 158.26 (Re=N-**C$_{Ph}$**), 173.11(C=S), 191.77(C=O). **FAB$^+$-MS** (m/z): 1032, [M + H]$^+$, 950, [M−Br]$^+$, 941, [M−PhN]$^+$.

4c (R^1, R^2 = Morph): Yield: 66 % (61 mg). Elemental analysis: Calcd. for $C_{36}H_{33}Br_2N_3OPSRe$: C, 45.56; H, 3.48; N, 4.43; S, 3.37. Found: C, 45.70; H, 3.41; N, 4.32; S, 3.41 %.

IR (KBr, cm^{-1}): 3051(w), 2862(w), 1508(s), 1485(s), 1435(s), 1396(vs), 1261(m), 1211(m), 1176(w), 1091(m), 1064(w), 1026(m), 995(w), 750(w), 694(s), 524(s). **^{1}H-NMR** (CDCl$_3$; ppm): 3.8−4.0 (m, 5H, CH$_2$), 4.14 (m, 1H, CH$_2$), 4.77 (m, 2H, CH$_2$), 7.1−7.7 (m, 25H, Ph). **^{31}P-NMR** (CDCl$_3$; ppm): 1.88 (s); **^{13}C-NMR** (CDCl$_3$; ppm): 48.79, 51.16 (CH$_2$-N), 66.51, 67.38 (CH$_2$-O), 121−134 (Ph), 172.24(C=S), 189.33(C=O).

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