



Rhenium(V) complexes with tridentate *P,N,S* ligands

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ABSTRACT

Novel, potentially tridentate ligands with *P,N,S* donor sets ($HL^{diethyl}$ and HL^{morph}) were prepared from reactions of *N*-(dialkyl)thiocarbamoylbenzimidide chlorides with 2-(diphenylphosphinomethyl)aniline. They readily react with $(NBu_4)[ReOCl_4]$ under formation of air-stable $[ReOCl_2(L^R)]$ complexes, in which the tridentate ligands coordinate meridionally. A similar coordination mode is observed in the nitridorhenium(V) complex $[ReN(OReO_3)(PPh_3)(L^{diethyl})]$, which can be obtained from a reaction of $[ReNCl_2(PPh_3)_2]$ and $HL^{diethyl}$. The complexes were characterized spectroscopically and by X-ray structure analyses.

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1. Introduction

Tri-, tetra- or multiple-dentate ligands, which form stable or kinetically inert complexes with rhenium and technetium are still of interest for nuclear medical labeling procedures, since previous studies have shown that mono- and bidentate ligand systems may suffer from insufficient *in vivo* stability due to rapid ligand exchange reactions with plasma components [1–5]. For common technetium(V) and rhenium(V) cores, ligands with ‘medium’ and ‘soft’ donor atoms are recommended [1,2]. Thus, chelators with a mixed phosphorus, sulfur and nitrogen donor sphere should be very suitable. However, there is surprisingly less known about rhenium or technetium complexes with such ligands. One example has been extensively studied. It is a thiolato-substituted amide, which has been prepared by a reaction of *N*-[2-(diphenylphosphanyl)]benzoyloxysuccinimide with *S*-(triphenylmethyl)-2-aminoethanethiol [6,7]. A more facile synthesis of *P,N,S* ligands is possible following a general procedure, which has been applied to various ligands including amino acid derivatives: reactions between *N*-(dialkyl)thiocarbamoylbenzimidoyl chlorides with substituted amines [8–13].

Since the first syntheses of *N*-(dialkyl)thiocarbamoylbenzimidoyl chlorides and their reaction products with primary amines, *N*-(dialkyl)thiocarbamoylbenzimidines [14,15], a large number of different transition metal complexes with such ligands were synthesized and extensively studied [16]. For a long time, however, this ligand system was restricted to bidentate ligands (*S,N* type ligands of Scheme 1). Recently, we extended the denticity of these

ligands up to four, so that nowadays *N*-(dialkyl)thiocarbamoylbenzimidines with *S,N,N,N*, *S,N,O*, *S,N,S* and *S,N,N,S* donor sets are available (Scheme 1), and their coordination chemistry with rhenium and is under study [8–13,17]. These compounds are known for a high flexibility in their donor functions and peripheral substituents as well as the formation of stable chelates with a number of metal ions.

As part of our systematic work in the synthesis of phosphine-containing ligands for rhenium and technetium, we report in the present work about reactions of 2-(diphenylphosphinomethyl)aniline with *N*-(dialkyl)thiocarbamoylbenzimidoyl chlorides, which yield potentially tridentate *P,N,S* ligands. Furthermore, we report about their coordination behavior towards oxorhenium(V) and nitridorhenium(V) centers.

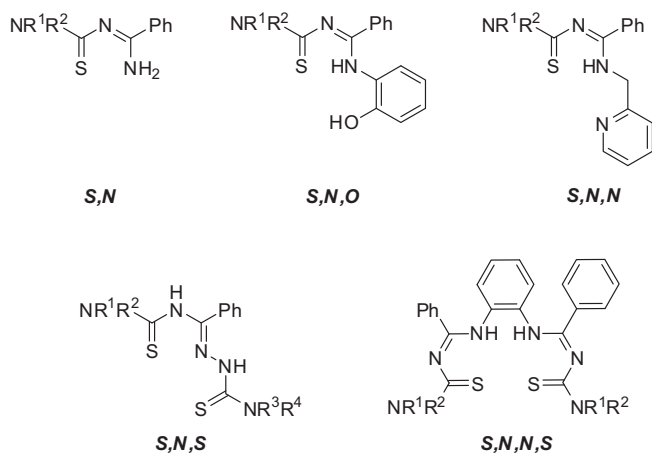
2. Results and discussion

Reactions of 2-(diphenylphosphinomethyl)aniline with substituted thiocarbamoylbenzimidoyl chlorides in tetrahydrofuran (Eq. (1)) give the tridentate ligands in good yields. Small amount (approximately 5%) of impurities due the formation of the corresponding phosphine oxides are formed during these reactions. They can be removed by subsequent recrystallization under anaerobic conditions in order to obtain the pure products. For complex formation with Re(V) compounds, however, the crude products can be used without purification, since the impurities have no influence on the desired complex formation and potential side-products such as phosphine oxide complexes do not play a role as long as a slight excess of the ligands is applied.

The $^{31}P\{^1H\}$ NMR spectra of $HL^{diethyl}$ and HL^{morph} reveal each one singlet at -17.3 ppm ($HL^{diethyl}$) and -16.9 ppm (HL^{morph}).

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^1H NMR spectra indicate hindered rotation around the C–N(alkyl) bonds, which can clearly be seen from the splitting patterns of the methylene and methyl signals of the morpholine and diethyl substituents. This is a common feature of the NMR spectra of this type of ligands and analogous coupling patterns were already described for similar thiocarbamoylbenzamidines. The IR spectra clearly show the vibration of the NH bonds at 3337 cm^{-1} (HL^{morph}) and 3325 cm^{-1} ($\text{HL}^{\text{diethyl}}$). Broad bands for the CN bonds are found at 1628 cm^{-1} (HL^{morph}) and 1612 cm^{-1} ($\text{HL}^{\text{diethyl}}$).

Reactions of HL^{R} with $(\text{NBu}_4)[\text{ReOCl}_4]$ result in green precipitates or crystals. The products have the composition $[\text{ReOCl}_2(\text{L}^{\text{R}})]$ (Eq. (2)). The organic ligand is single deprotonated and coordinates meridionally tridentate in the equatorial coordination sphere of rhenium via the phosphorus, nitrogen and sulfur donor atoms. The remaining two positions are occupied by chlorido ligands.

The $^31\text{P}\{^1\text{H}\}$ NMR spectra of both compounds each show a singlet. The signals appear at 5.7 ppm for $[\text{ReOCl}_2(\text{L}^{\text{diethyl}})]$ and at 7.1 ppm for $[\text{ReOCl}_2(\text{L}^{\text{morph}})]$. This indicates a low-field shift of more than 20 ppm with respect to the signals observed in the spectra of the non-coordinated ligands, and confirms the presence of only one phosphorus atom in the complexes. The ^1H NMR spectra of both compounds are complex, which is due to hindered rotation around the C–NR 1 R 2 bonds as has already been described for the uncoordinated benzamidines $\text{HL}^{\text{diethyl}}$ and HL^{morph} . This feature is also common for metal complexes with thiocarbamoylbenzamidines and leads to a splitting of the signals of the alkyl groups of the diethyl and morpholine substituents. Two multiplets can be assigned to the two methyl groups at 1.38 ppm in the case of $(\text{L}^{\text{diethyl}})^-$, whereas the two methylene groups in this ligand are splitted into four signals at 3.58, 3.81, 4.49 and 4.99 ppm. In case of $(\text{L}^{\text{morph}})^-$, five multiplets at 3.80, 4.21, 4.39, 4.75 and 5.20 ppm can be assigned to the methylene groups of the morpholine substituent. The methylene protons adjacent to the phosphorus atoms produce multiplets at 4.28 ppm ($[\text{ReOCl}_2(\text{L}^{\text{diethyl}})]$) and 4.39 ppm ($[\text{ReOCl}_2(\text{L}^{\text{morph}})]$), respectively. The latter one overlaps with a signal of one of the methylene groups of the morpholine substituent.

The IR spectra of both complexes confirm the deprotonation of the organic ligands by the absence of ν_{NH} vibrations. Strong, broad bands can be assigned to the C=N double bonds of the organic ligands in both cases. Both bands, which are found at 1523 cm^{-1} for $[\text{ReOCl}_2(\text{L}^{\text{diethyl}})]$ and at 1512 cm^{-1} for $[\text{ReOCl}_2(\text{L}^{\text{morph}})]$ are bathochromically shifted by approximately 100 cm^{-1} with respect to $\text{HL}^{\text{diethyl}}$ and HL^{morph} . These shifts indicate chelate formation with a large degree of π -electron delocalization within the chelate rings.

Crystals suitable for X-ray diffraction were obtained by crystallization from a mixture of $\text{CH}_2\text{Cl}_2/\text{acetone}$ or pure acetone. $[\text{ReOCl}_2(\text{L}^{\text{diethyl}})]$ crystallizes in the orthorhombic space group $Fdd2$

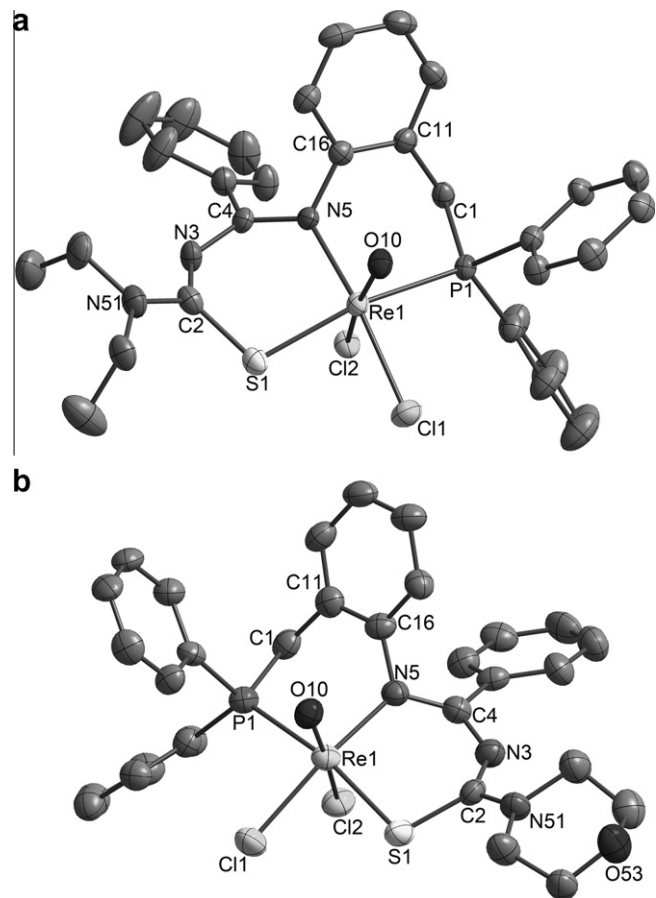


Fig. 1. Ellipsoid representation [31] of the molecular structure of (a) $[\text{ReO}-\text{Cl}_2-(\text{L}^{\text{diethyl}})]$ and (b) $[\text{ReOCl}_2(\text{L}^{\text{morph}})]$. Thermal ellipsoids represent 50% probability. H atoms have been omitted for clarity.

Table 1
Selected bond lengths (Å) and angles ($^\circ$) in $[\text{ReOCl}_2(\text{L}^{\text{diethyl}})]$ and $[\text{ReOCl}_2(\text{L}^{\text{morph}})]$.

	$[\text{ReOCl}_2(\text{L}^{\text{diethyl}})]$	$[\text{ReOCl}_2(\text{L}^{\text{morph}})]$
Re1–O10	1.685(4)	1.671(6)
Re1–C11	2.401(2)	2.399(2)
Re1–C12	2.466(2)	2.482(2)
Re1–S1	2.344(2)	2.333(2)
Re1–N5	2.084(5)	2.086(7)
Re1–P1	2.461(2)	2.452(2)
C2–N3	1.328(8)	1.33(2)
C2–N51	1.330(7)	1.330(7)
N3–C4	1.316(7)	1.32(2)
C4–N5	1.356(7)	1.36(2)
N5–C16	1.424(7)	1.44(2)
N5–Re1–CH	169.4(7)	170.1(2)
SI–Re1–PI	163.80(5)	164.48(9)
O10–Re1–C12	163.3(2)	166.8(2)
C11–Re1–C12	87.92(5)	87.55(9)

with one molecule in the asymmetric unit, whereas $[\text{ReOCl}_2(\text{L}^{\text{morph}})]$ crystallizes in the monoclinic space group $P2_1/c$ with one complex molecule and two molecules of solvent acetone in the asymmetric unit. Ellipsoid representations of the complex molecules are shown in Fig. 1. Selected bond lengths and angles for both compounds are given in Table 1.

The *trans* influence of the oxo ligand lengthens the Re–Cl2 bonds to values of 2.466(2) and 2.482(2) Å, respectively, in comparison to approximately 2.40 Å for the Re1–C11 bonds in the equatorial coordination spheres. Inside the organic ligands, a bond

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