



Tricarbonyltechnetium(I) and -rhenium(I) complexes with *N'*-thiocarbamoylpicolylbenzamidines

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ABSTRACT

N,N-Dialkylamino(thiocarbonyl)-*N'*-picolylbenzamidines react with $(\text{NEt}_4)_2[\text{M}(\text{CO})_3\text{X}_3]$ ($\text{M} = \text{Re}$, $\text{X} = \text{Br}$; $\text{M} = \text{Tc}$, $\text{X} = \text{Cl}$) under formation of neutral $[\text{M}(\text{CO})_3\text{L}]$ complexes in high yields. The monoanionic NNS ligands bind in a facial coordination mode and can readily be modified at the $(\text{CS})\text{NR}^1\text{R}^2$ moiety. The complexes $[\text{Re}(\text{CO})_3(\text{L}^{\text{PyMor}})]$ and $[\text{Re}(\text{CO})_3(\text{L})]$ ($\text{L} = \text{L}^{\text{PyMor}}$, L^{PyEt}) were characterized by X-ray diffraction. Reactions of $[\text{Re}(\text{CO})_3(\text{H}_2\text{O})_3]^+$ with the *N'*-thiocarbamoylpicolylbenzamidines give the corresponding $^{99\text{m}}\text{Tc}$ complexes. The ester group in $\text{HL}^{\text{PyCOOEt}}$ allows linkage between biomolecules and the metal core.

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1. Introduction

The radionuclides of technetium and rhenium play an important role in the field of nuclear medicine [1–3]. $^{99\text{m}}\text{Tc}$ (pure γ -emitter, $E_\gamma = 140$ keV, $t_{1/2} = 6$ h) is the most used isotope for diagnostic radiopharmaceuticals [2]. The β -emitting rhenium isotopes ^{186}Re and ^{188}Re are under consideration as therapeutic agents for various forms of cancer or arthritis [3]. One focus of recent research in this field is the radiolabelling of biomolecules or pharmacophores, which rapidly and efficiently transport the radionuclide to the target site. The most common way to incorporate the radiometals is the use of a strong chelator which coordinates the metal and serves at the same time as linker to the biomolecule [4]. The tricarbonyl complexes $[\text{M}(\text{CO})_3(\text{H}_2\text{O})_3]^+$ ($\text{M} = ^{99\text{m}}\text{Tc}$, ^{99}Tc , Re) are excellent starting materials for this purpose. A low-pressure synthesis of $[\text{M}(\text{CO})_3(\text{H}_2\text{O})_3]^+$ ($\text{M} = ^{99\text{m}}\text{Tc}$, ^{99}Tc , Re) has been developed which can be performed in aqueous media [5]. The three aqua ligands can easily be replaced by chelating ligands while the facial binding carbonyl ligands are largely inert against ligand exchange. Suitable ligand systems for the $[\text{M}(\text{CO})_3]^+$ core should preferably be monoanionic, tridentate and facial coordinating in order to form neutral complexes, which are thermodynamically stable and kinetically inert.

Recently, the synthesis of a number of tridentate derivatives of *N,N*-[(dialkylamino)-*N'*-(thiocarbonyl)]benzamidines, such as the

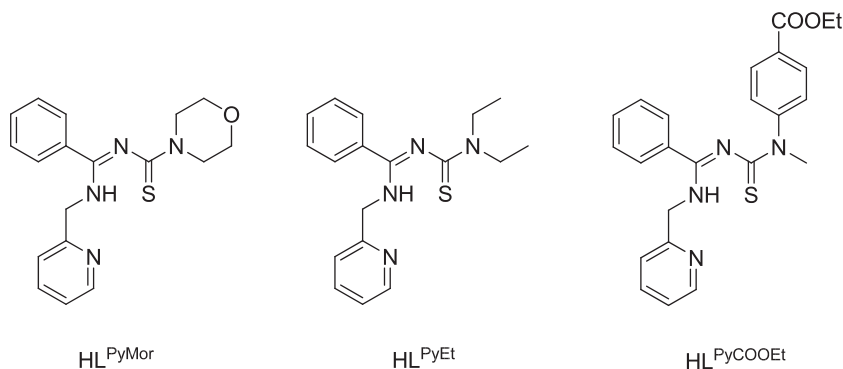
compounds shown in Scheme 1, have been reported. They are prepared by reactions of benzimidoyl chlorides with functionalized amines [6], and can readily be varied in their periphery which helps to tune their properties or couple them to biomolecules [7]. The coordination chemistry of such ligands with technetium(V) and rhenium(V) cores has been extensively studied [6–8]. Similar complexes with the $[\text{M}(\text{CO})_3]^+$ core are only known with bidentate *N*-[(dialkylamino)(thiocarbonyl)]benzamidines up to now [9].

2. Results and discussion

Reactions of $(\text{NEt}_4)_2[\text{Re}(\text{CO})_3\text{Br}_3]$ with 1 eq. HL^{PyMor} or HL^{PyEt} give $[\text{Re}(\text{CO})_3(\text{L})]$ ($\text{L} = \text{L}^{\text{PyMor}}$, L^{PyEt}) complexes in almost quantitative yields. The ESI^+ mass spectra of the products show intense signals corresponding to the expected $[\text{M}+\text{H}]^+$ ions. The spectrum of $[\text{Re}(\text{CO})_3(\text{L}^{\text{PyMor}})]$ displays an extra peak for the $[\text{M}+\text{Na}]^+$ ion. Infrared spectra of both complexes show the typical pattern for a facial arrangement of CO ligands ($\nu_{\text{C=O}}$: 2206, 1906 and 1865 cm^{-1} for $[\text{Re}(\text{CO})_3(\text{L}^{\text{PyMor}})]$; 2009, 1899 and 1884 cm^{-1} for $[\text{Re}(\text{CO})_3(\text{L}^{\text{PyEt}})]$). The $\nu_{\text{C=N}}$ stretches are bathochromically shifted with respect to those of the non-coordinated benzamidines from 1620 to 1607 cm^{-1} for $[\text{Re}(\text{CO})_3(\text{L}^{\text{PyMor}})]$ and 1605 cm^{-1} for $[\text{Re}(\text{CO})_3(\text{L}^{\text{PyEt}})]$. These shifts are relatively small compared to those, which were observed for rhenium(V) and technetium(V) complexes (up to 120 cm^{-1}) [6]. Apparently, the large degree of π -electron delocalization within the chelate rings, which results in large bathochromic shifts in the IR spectra and an almost perfect C–N

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Scheme 1. Ligands used throughout this paper.

bond-length equalization in the rhenium(V) and technetium(V) complexes does not apply to $[\text{Re}(\text{CO})_3(\text{L})]$ ($\text{L} = \text{L}^{\text{PyMor}}, \text{L}^{\text{PyEt}}$) due to the facial coordination of the tridentate ligands. The ^{13}C NMR spectrum of $[\text{Re}(\text{CO})_3(\text{L}^{\text{PyMor}})]$ shows three signals for the carbon atoms of the carbonyl ligands at 198.8, 196.4 and 193.3 ppm, reflecting some influence of the trans-bonded donor atoms. For the other compounds, unfortunately, ^{13}C NMR of satisfactory quality could not be obtained due to their lower solubility.

The technetium complex $[\text{Re}(\text{CO})_3(\text{L}^{\text{PyMor}})]$ was synthesized from $(\text{NEt}_4)_2[\text{Re}(\text{CO})_3\text{Cl}_3]$ and HL^{PyMor} in methanol. Its infrared spectrum shows the $\nu_{\text{C}=\text{N}}$ stretch at 1609 cm^{-1} and the bands of the CO ligands at 2017, 1921 and 1886 cm^{-1} . The absence of absorptions in the regions around 3350 and 3400 cm^{-1} (in which the ν_{NH} stretch is detected in the spectrum of the uncoordinated HL^{PyMor}) indicates the expected deprotonation of the ligand during complex formation. The ^{99}Tc NMR spectrum shows a signal at -1220 ppm with a half-width of 596 Hz ($(\text{NEt}_4)_2[\text{Re}(\text{CO})_3\text{Cl}_3]$: $\delta = -870\text{ ppm}$, $\Delta\nu_{1/2} = 29\text{ Hz}$ in H_2O).

Single crystals of $[\text{Re}(\text{CO})_3(\text{L}^{\text{PyMor}})]$, $[\text{Re}(\text{CO})_3(\text{L}^{\text{PyEt}})]$ and $[\text{Re}(\text{CO})_3(\text{L}^{\text{PyCOOEt}})]$ were obtained either directly from the reaction solutions or by recrystallization of the initially formed pale-yellow powders from acetone. Fig. 1 illustrates the molecular structure of $[\text{Re}(\text{CO})_3(\text{L}^{\text{PyMor}})]$. Since the structure of $[\text{Re}(\text{CO})_3(\text{L}^{\text{PyMor}})]$ is virtually identical, no extra figure is presented for the rhenium compound. The structure of $[\text{Re}(\text{CO})_3(\text{L}^{\text{PyEt}})]$ is shown in Fig. 2. Selected bond lengths and angles of all three complexes are presented in Table 1. The metal atoms show distorted octahedral coordination

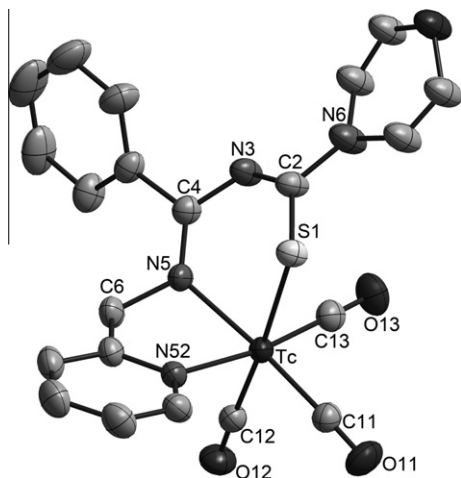


Fig. 1. Ellipsoid representation [16] of the molecular structure of $[\text{Re}(\text{CO})_3(\text{L}^{\text{PyMor}})]$. Thermal ellipsoids represent 50% probability. H atoms have been omitted for clarity.

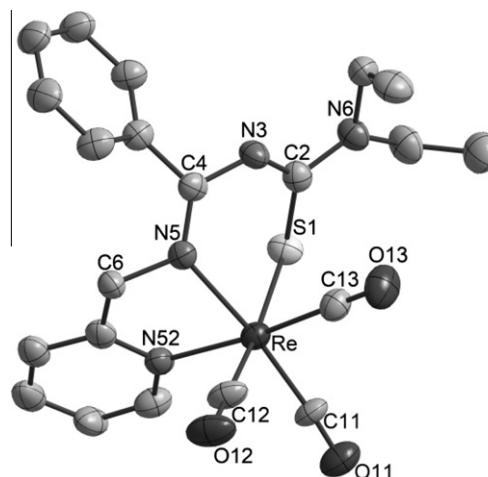


Fig. 2. Ellipsoid representation [16] of the molecular structure of $[\text{Re}(\text{CO})_3(\text{L}^{\text{PyEt}})]$. Thermal ellipsoids represent 50% probability. H atoms have been omitted for clarity.

Table 1

Selected bond lengths (Å) and angles ($^\circ$) in $[\text{Re}(\text{CO})_3(\text{L}^{\text{PyMor}})]$, $[\text{Re}(\text{CO})_3(\text{L}^{\text{PyEt}})]$ and $[\text{Re}(\text{CO})_3(\text{L}^{\text{PyCOOEt}})]$.

	$[\text{Re}(\text{CO})_3(\text{L}^{\text{PyMor}})]$	$[\text{Re}(\text{CO})_3(\text{L}^{\text{PyEt}})]$	$[\text{Re}(\text{CO})_3(\text{L}^{\text{PyCOOEt}})]$
M–C11	1.933(3)	1.938(4)	1.934(7)
M–C12	1.911(2)	1.909(4)	1.932(8)
M–C13	1.909(3)	1.923(4)	1.932(8)
M–S1	2.4895(7)	2.491(2)	2.500(2)
M–N5	2.141(2)	2.143(3)	2.136(6)
M–N52	2.177(2)	2.176(3)	2.180(6)
S1–C2	1.750(2)	1.754(4)	1.755(8)
C2–N3	1.324(3)	1.322(5)	1.32(1)
C2–N6	1.378(4)	1.384(7)	1.35(1)
N3–C4	1.360(3)	1.351(5)	1.36(1)
C4–N5	1.298(3)	1.307(5)	1.32(1)
N5–C6	1.474(3)	1.469(5)	1.46(1)
C11–M–N5	172.00(9)	171.2(2)	170.5(3)
C11–M–C12	88.4(1)	88.7(2)	89.4(3)
S1–M–N5	81.34(5)	81.0(1)	81.3(2)
N5–M–N52	74.99(7)	74.3(1)	74.5(2)
M–S1–C2	97.77(8)	97.5(1)	96.9(3)
S1–C2–N3	127.9(2)	127.8(3)	126.6(6)
C2–N3–C4	124.1(2)	124.3(3)	124.1(7)
N3–C4–N5	125.4(2)	125.4(3)	125.2(7)
C4–N5–C6	122.6(2)	122.4(3)	121.2(6)
M–N5–C4	127.5(2)	127.4(3)	127.7(5)

dination spheres with facially bonded carbonyl ligands. The remaining three coordination positions are occupied by the singly deprotonated organic ligands. The chelate rings are strongly

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