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Rhenium and Technetium Complexes with Tridentate *N*-[(*N*′,*N*′-Dialkylamino)(thiocarbonyl)]-*N*′-substituted Benzamidine Ligands

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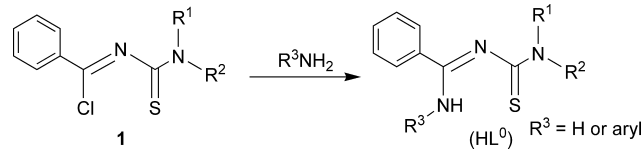
N-[(Dialkylamino)(thiocarbonyl)]benzimidoyl chlorides react with functionalized amines such as 2-aminophenol, 2-methylaminopyridine, and 2-aminobenzoic acid in clean and high-yield procedures with the formation of the novel tridentate *N*-[(*N*′,*N*′-dialkylamino)(thiocarbonyl)]-*N*′-substituted benzamidine ligands H_2L^1, HL^2, and H_2L^3. By starting from $(NBu_4)[MOCl_4]$ (M = Re, Tc) or $[ReOCl_3(PPh_3)_2]$ and H_2L^1, a series of oxorhenium(V) and oxotechnetium(V) complexes of the composition $[MOCl(L^1)]$ were synthesized and characterized by spectroscopic methods and X-ray crystallography. The monomeric, five-coordinate compounds are air-stable and bind $(L^1)^{2-}$ tridentate in the equatorial coordination sphere. Dimeric products of the compositions $[\{ReOCl(L^2)\}_2O]$ and $[ReOCl(L^3)]_2$ were isolated during reactions with HL^2 and H_2L^3. While dimerization in $[\{ReOCl(L^2)\}_2O]$ is established via an oxo bridge, the metal atoms in $[ReOCl(L^3)]_2$ are connected by the carboxylic group of the ligand, and the product represents the first example of a high-oxidation state rhenium complex displaying such a bonding feature.

Introduction

Since *N*-[(dialkylamino)(thiocarbonyl)]benzimidoyl chlorides (**1**) were first synthesized and incorporated into the synthesis of corresponding benzamidines,[1,2] numerous bidentate dialkylaminothiocarbonylbenzamidine ligands (HL^0) have been synthesized, and their coordination chemistry with transition metal ions such as Ni^{2+}, Pd^{2+}, Pt^{2+}, Co^{3+}, Cu^{2+}, Ag^+, and Au^+ has been extensively studied.[3] With technetium and rhenium, dialkylaminothiocarbonylbenzamidines HL^0 (R^3 = H, aryl) act as versatile ligands and stabilize various cores such as $[M{=}O]^{3+}$,[4] $[M{\equiv}N]^{2+}$,[5] and $[M(CO)_3]^+$ (M = Re, Tc).[6] In most of the known examples, they bind as mononegative, bidentate ligands.



In principle, the general synthetic procedure of the ligand class HL^0, in which benzimidoyl chlorides react with ammonia or primary aromatic amines, should also be well suitable for reactions with other, functionalized primary amines as well as secondary amines. This, however, has only

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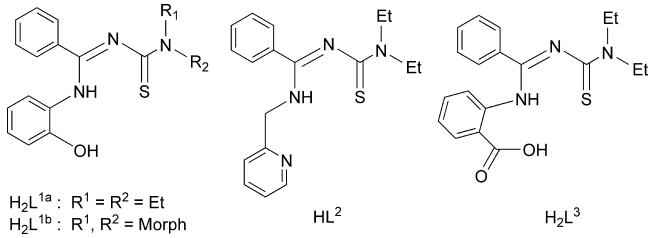
Chart 1. Ligands Used in This Study



H_2L^{1a}: $R^1 = R^2 = Et$
H_2L^{1b}: $R^1, R^2 = Morph$

HL^2

H_2L^3

been demonstrated for a small number of amino acid esters,[7] diamines,[8] and tris(aminoethyl)amine.[9] Furthermore, no metal complexes of the newly proposed tridentate ligands have hitherto been isolated and structurally characterized. Only two structural reports of Cu(II) and Ni(II) with tetradentate benzamidinates exist.[8]

Here, we introduce the syntheses of novel, tridentate dialkylamino(thiocarbonyl)benzamidine ligands and some of their rhenium and technetium complexes. These new ligands (Chart 1) are the first representatives of a novel family of multidentate systems, which are primarily intended as strong chelators in the radiopharmaceutical chemistry of technetium and the radioactive rhenium isotopes ^{186}Re and ^{188}Re.[10] In addition, these multidentate systems should also be of interest in the complexation of other transition metal ions.

Experimental Section

Materials. All reagents used in this study were reagent grade and used without further purification. The solvents were dried and used freshly distilled prior to use unless otherwise stated. $(NBu_4)[ReOCl_4]$, $(NBu_4)[TcOCl_4]$, and $[ReOCl_3(PPh_3)_2]$ were prepared by standard procedures.[11] The syntheses of the *N*-[(dialkylamino)(thiocarbonyl)]benzimidoyl chlorides were performed by the standard procedure of Beyer and Widera.[1]

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 beta emission of the technetium compounds. Secondary X-rays (bremsstrahlung) play an important role only when larger amounts of ^{99}Tc are used.

Physical Measurements. IR 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, positive electrospray ionization mass spectra (ESI-MS) were measured with a Agilent 6210 ESI-TOF (Agilent Technologies), and electron-impact (EI) mass spectra were measured with a Varian MAT711 (60 °C, 70 eV) mass spectrometer. All MS results are given in the following form: *m*/*z*, assignment. The elemental analysis of carbon, hydrogen, nitrogen, and sulfur was determined using a Heraeus vario EL elemental analyzer. The ^{99}Tc values were determined by standard liquid scintillation counting. NMR spectra were taken with a JEOL 400 MHz multinuclear spectrometer.

Syntheses of the Ligands. *N*-(*N*″,*N*″-Dialkylaminothiocarbonyl)-*N*′-(2-hydroxyphenyl)benzamidines, H_2L^1. *N*-(*N*′,*N*′- Dialkylaminothiocarbonyl)benzimidoyl chloride (5 mmol) was dissolved in 10 mL of dry acetone and slowly added to a stirred mixture of 2-aminophenol (545 mg, 5 mmol) and NEt_3 (1.51 g, 15 mmol) in 10 mL of dry acetone. The mixture was stirred for 2 h at 40 °C and then cooled to 0 °C. The formed precipitate of $NEt_3 \cdot HCl$ was filtered off, and the filtrate was evaporated under reduced pressure. The resulting residue was redissolved in 4 mL of MeOH. Diethylether (10 mL) was added, and the mixture was stored at −20 °C. The pale yellow solid of H_2L^1, which deposited from this solution over a period of two days, was filtered off, washed with diethylether, and dried under vacuum. The resulting compounds were used for the synthesis of the complexes without further purification.

Data for H_2L^{1a} ($R^1 = R^2 = Et$) (2a). Yield: 78% (1.275 g). Anal. Calcd for $C_{18}H_{21}N_3OS$: C, 66.06; H, 6.42; N, 12.84; S, 9.79%. Found: C, 65.80; H, 6.40; N, 13.22; S, 9.02%. IR (ν in cm^{-1}): 3421 m (N—H), 3060 m, br (O—H), 1620 s (C═N). ^{1}H NMR ($CDCl_3$; δ, ppm): 1.21 (t, $J = 7.1$ Hz, 3 H, CH_3), 1.32 (t, $J = 7.3$ Hz, 3 H, CH_3), 3.69 (q, $J = 7.2$ Hz, 2 H, CH_2), 3.87 (q, $J = 7.1$ Hz, 2H, CH_2), 6.60 (t, $J = 6.9$ Hz, 1 H, PhOH), 6.86 (d, $J = 6.7$ Hz, 1 H, PhOH), 6.89 (t, $J = 6.4$ Hz, 1 H, PhOH), 7.04 (d, $J = 7.5$ Hz, 1 H, PhOH), 7.24 (t, $J = 7.5$ Hz, 2 H, Ph), 7.33 (t, $J = 7.4$ Hz, 1 H, Ph), 7.43 (d, $J = 7.2$ Hz, 2 H, Ph). ^{13}C NMR ($CDCl_3$; δ, ppm): 12.01, 13.45 (CH_3), 46.01, 46.17 (CH_2), 116.89, 120.00, 126.27, 126.94, 127.60, 128.24, 128.54, 128.90, 130.67, and 134.53 (Ph + PhOH), 149.36 (C═N), 187.06 (C═S).

Data for H_2L^{1b} (R^1, R^2 = Morph) (2b). Yield: 80% (1.364 g). Anal. Calcd for $C_{18}H_{19}N_3O_2S$: C, 63.34; H, 5.61; N, 12.32; S, 9.38%. Found: C, 60.60; H, 6.4; N, 12.67; S, 9.10%. IR (ν in cm^{-1}): 3367 m (N—H), 3051 m, br (O—H), 1612 s (C═N). ^{1}H NMR ($CDCl_3$; δ, ppm): 3.63 (t, $J = 4.8$ Hz, 2 H, N—CH_2), 3.69 (t, $J = 4.7$ Hz, 2 H, N—CH_2), 3.93 (t, $J = 4.8$ Hz, 2 H, O—CH_2), 4.14 (t, $J = 4.8$ Hz, 2 H, O—CH_2), 6.66 (t, $J = 7.6$ Hz, 1 H, PhOH), 6.86 (d, $J = 7.4$ Hz, 1 H, PhOH), 6.93 (t, $J = 7.7$ Hz, 1 H, PhOH), 7.00 (d, $J = 8.0$ Hz, 1 H, PhOH), 7.28 (t, $J = 7.5$ Hz, 2 H, Ph), 7.37 (t, $J = 7.4$ Hz, 1 H, Ph), 7.44 (d, $J = 7.7$ Hz, 2 H, Ph). ^{13}C NMR ($CDCl_3$; δ, ppm): 48.06, 48.70 (N—CH_2), 65.99, 66.51 (O—CH_2), 117.29, 120.50, 124.60, 127.00, 127.63, 128.40, 128.49, 128.92, 131.04, and 134.24 (Ph + PhOH), 149.45 (C═N), 187.57 (C═S). EI MS (*m*/*z*): 341 (49%, M^+), 255 (30%, M − Morph), 233 (35%, M − Ph(OH)NH).

***N*-(*N*″,*N*″-Diethylaminothiocarbonyl)-*N*′-picolylbenzamidine, HL^2 (3).** A solution of *N*-(*N*′,*N*′-diethylaminothiocarbonyl)-benzimidoyl chloride (1.018 g, 4 mmol) in 10 mL of dry acetone was added dropwise to a mixture of 2-methylaminopyridine (436 mg, 4 mmol) and triethylamine (606 mg, 6 mmol) in 5 mL of dry acetone over a period of 5 min. After a few minutes, a colorless precipitate of $NEt_3 \cdot HCl$ began to deposit. The mixture was stirred for 2 h and then cooled to 0 °C. The formed precipitate of $NEt_3 \cdot HCl$ was filtered off, and the solvent was removed under vacuum. The resulting residue was recrystallized from methanol to obtain pale yellow crystals of HL^2. Yield: 85% (1.108 g) Anal. Calcd for $C_{18}H_{22}N_4S$: C, 66.26; H, 6.75; N, 17.18; S, 9.82%. Found: C, 65.72; H, 6.58; N, 16.82; S, 9.05%. IR (ν in cm^{-1}): 3217 m (N—H), 1608 s (C═N). ^{1}H NMR ($CDCl_3$; δ, ppm): 1.18 (t, $J = 7.0$ Hz, 3 H, CH_3),

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1.25 (t, $J = 7.0$ Hz, 3 H, CH_3), 3.64 (q, $J = 7.0$ Hz, 2 H, CH_2), 3.93 (q, $J = 7.0$ Hz, 2 H, CH_2), 4.73 (s, 2 H, CH_2—Py), 7.21 (t, $J = 6.1$ Hz, 1 H, Py), 7.38−7.45 (m, 4 H, Ph + Py), 7.52 (d, $J = 6.8$ Hz, 2 H, Ph), 7.70 (t, $J = 7.5$ Hz, 1 H, Py), 8.53 (d, $J = 4.8$ Hz, 1 H, Py).

***N*-(*N*″,*N*″-Diethylaminothiocarbonyl)-*N*′-(2-carboxyphenyl)-benzamidine, H_2L^3 (4).** H_2L^3 was synthesized by a procedure similar to that of the method described for H_2L^1 except that 2-aminobenzoic acid was used instead of 2-aminophenol. Yield: 40% (711 mg). Anal. Calcd for $C_{19}H_{21}N_3O_2S$: C, 64.23; H, 5.92; N, 11.83; S, 9.01%. Found: C, 64.61; H, 5.81; N, 11.73; S, 10.33%. IR (ν in cm^{-1}): 3163 m, br (O—H), 1682 s (C═O), 1635 s (C═N). ^1H NMR ($CDCl_3$; δ, ppm): 1.2−1.4 (m, 6 H, CH_3), 3.4−4.0 (m, 4 H, CH_2), 5.78 (s, br, 1 H, NH), 7.3−7.6 (m, 6 H, Ph + PhCOOH), 7.63 (t, $J = 8.1$ Hz, 1 H, PhCOOH), 7.78 (t, $J = 7.2$ Hz, 1 H, PhCOOH), 8.25 (t, $J = 8.0$ Hz, 1 H, PhCOOH).

Syntheses of Complexes. [ReO(L^1)Cl] (5). HL^1 (0.11 mmol) dissolved in 3 mL of MeOH was added dropwise to a stirred solution of $(NBu_4)[ReOCl_4]$ (58 mg, 0.1 mmol) in 2 mL of MeOH. The color of the solution immediately turned to deep red, and a red precipitate deposited within 30 min. The red powder was filtered off, washed with cold methanol, and recrystallized from CH_2Cl_2/MeOH.

Data for 5a. Yield: 87% (49 mg). Anal. Calcd for $C_{18}H_{19}ClN_3O_2SRe$: C, 38.33; H, 3.38; N, 7.46; S, 5.69%. Found: C, 38.49; H, 3.41; N, 7.08; S, 5.63%. IR (ν in cm^{-1}): 1527 vs (C═N), 991 s (Re═O). ^1H NMR ($CDCl_3$; δ, ppm): 1.34 (t, $J = 7.6$ Hz, 3 H, CH_3), 1.38 (t, $J = 7.6$ Hz, 3 H, CH_3), 3.80 (m, 1 H, CH_2), 3.84 (m, 1 H, CH_2), 4.21 (m, 1 H, CH_2), 4.43 (m, 1 H, CH_2), 6.5−6.6 (m, 2 H, PhOH), 6.85 (t, $J = 7.3$ Hz, 1 H, PhOH), 7.26 (d, $J = 7.4$ Hz, 1 H, PhOH), 7.36 (t, $J = 7.7$ Hz, 2 H, Ph), 7.49 (t, $J = 7.4$ Hz, 1 H, Ph), 7.68 (d, $J = 7.3$ Hz, 2 H, Ph). ^{13}C NMR ($CDCl_3$; δ, ppm): 13.20, 13.32 (CH_3), 47.80, 48.57 (CH_2), 116.79, 117.69, 120.64, 124.55, 128.99, 130.63, 133.25 (Ph + PhOH), 145.12 (C_{PhOH}—N), 165.26, (C_{PhOH}—O), 165.18 (C═N), 173.98 (C═S). Positive ESI-MS (m/z): 560 (50%, $[M - Cl + MeOH]^+$), 528 (5%, $[M - Cl]^+$.

Data for 5b. Yield: 83% (48 mg). Anal. Calcd for $C_{18}H_{17}ClN_3O_3SRe$: C, 37.45; H, 2.95; N, 7.28; S, 5.55%. Found: C, 37.41; H, 2.83; N, 7.40; S, 5.39%. IR (ν in cm^{-1}): 1527 vs (C═N), 995 s (Re═O). ^1H NMR ($CDCl_3$; δ, ppm): 3.7−4.1 (m, 4 H, N—CH_2), 4.2−4.5 (m, 4 H, O—CH_2), 6.56 (t, $J = 7.8$ Hz, 1 H, PhOH), 6.61 (d, $J = 7.0$ Hz, 1 H, PhOH), 6.93 (t, $J = 6.6$ Hz, 1 H, PhOH), 7.32 (d, $J = 7.6$ Hz, 1 H, PhOH), 7.43 (t, $J = 7.8$ Hz, 2 H, Ph), 7.55 (t, $J = 7.4$ Hz, 1 H, Ph), 7.73 (d, $J = 7.3$ Hz, 2 H, Ph). ^{13}C NMR ($CDCl_3$; δ, ppm): 50.20, 50.41 (N—CH_2), 66.53, 66.57 (O—CH_2), 116.93, 117.95, 120.70, 124.98, 129.04, 130.77, 133.11, 133.56 (Ph + PhOH), 144.82 (C_{PhOH}—N), 166.48 (C_{PhOH}—O), 165.4 (C═N), 172.26 (C═S). Positive ESI-MS (m/z): 574 (100%, $[M - Cl + MeOH]^+$), 542 (5%, $[M - Cl]^+$.

X-ray quality single crystals of **5b** were obtained by slow evaporation of a CH_2Cl_2/isopropanol solution.

[TcO(L^{1a})Cl] (6a). The technetium complex was prepared from $(NBu_4)[TcOCl_4]$ by the procedure described previously for its rhenium analogue. Single crystals of **6a** suitable for X-ray analysis were obtained by slow evaporation of a CH_2Cl_2/isopropanol solution. Yield: 86% (41 mg). Anal. Calcd for $C_{18}H_{19}ClN_3O_2STc$: Tc, 20.8%. Found: Tc, 19.9%. IR (ν in cm^{-1}): 1524 vs (C═N), 972 s (Tc═O). ^1H NMR ($CDCl_3$; δ, ppm): 1.42 (m, 6 H, CH_3), 3.89 (m, 2 H, CH_2), 4.12 (m, 1 H, CH_2), 4.27 (m, 1 H, CH_2), 6.5−6.6 (m, 2 H, PhOH), 6.91 (t, $J = 7.5$ Hz, 1 H, PhOH), 7.25 (d, $J = 7.4$ Hz, 1 H, PhOH), 7.40 (t, $J = 7.1$ Hz, 2 H, Ph), 7.54 (t, $J = 7.3$ Hz, 1 H, Ph), 7.70 (d, $J = 7.7$ Hz, 2 H, Ph).

[ReO(L^{1a})(gly)] (7). Method 1. HL^{1a} (33 mg, 0.1 mmol) in 3 mL of MeOH was added to a solution of $(NBu_4)[ReOCl_4]$ (58 mg, 0.1 mmol) in 3 mL of CH_2Cl_2. After stirring at room temperature for 15 min, solid glycine (8.2 mg, 0.11 mmol) and three drops of NEt_3 were added, and the mixture was heated under reflux for 3 h. This resulted in a complete dissolution of glycine and the formation of a dark red solution. The solvent was removed under vacuum, and the residue was washed with cold methanol and recrystallized from CH_2Cl_2/MeOH to yield big red crystals of **7** suitable for X-ray diffraction.

Method 2. Glycine (8.2 mg, 0.11 mmol), three drops of NEt_3, and **5a** (57 mg, 0.1 mmol) were heated under reflux in a CH_2Cl_2/MeOH mixture (1/1) (10 mL) for 3 h, whereupon glycine completely dissolved. The volume of the mixture was reduced to approximately 2 mL, and the red solid, which precipitated upon cooling to room temperature, was filtered off, subsequently washed with cold MeOH, and dried under vacuum. Yield: 73% (44 mg) for method 1, 80% (48 mg) for method 2. Anal. Calcd for $C_{20}H_{23}N_4O_4SRe$: C, 39.92; H, 3.83; N, 9.31; S, 5.32%. Found: C, 40.61; H, 3.68; N, 10.09; S, 5.73%. IR (ν in cm^{-1}): 3425 m (N—H), 1651 vs (C═O), 1543 vs (C═N), 972 s (Re═O). ^1H NMR ($CDCl_3$; δ, ppm): 1.25−1.31 (m, 6 H, CH_3), 3.50 (m, 1 H, CH_2), 3.86 (m, 2 H, CH_2), 3.9−4.1 (m, 1 $H_{\alpha\text{-}CH2}$ + 2 H_{CH2}), 5.87 (bs, 1 H, NH_2), 6.28 (t, $J = 7.0$ Hz, 1 H, PhOH), 6.36 (d, $J = 6.8$ Hz, 1 H, PhOH), 6.85 (bs, 1 H_{PhOH} + 1 H_{NH2}), 6.95 (d, $J = 7.7$ Hz, 1 H, PhOH), 7.30 (t, $J = 7.3$ Hz, 2 H, Ph), 7.35 (t, $J = 7.2$ Hz, 1 H, Ph), 7.57 (d, $J = 6.9$ Hz, 2 H, Ph). ^{13}C NMR ($CDCl_3$; δ, ppm): 13.41 (CH_3), 47.42, 47.81 (CH_2), 61.91 (α-CH_2, glycine), 116.98, 118.92, 120.83, 125.24, 128.40, 130.55, 131.54, and 134.90 (Ph + PhOH), 146.96 (C_{PhOH}—N), 164.43 (C_{PhOH}—O), 167.88 (C═N), 174.34 (C═S), 177.28 (C═O). FAB^+ MS (m/z): 602, 36% $[M + H]^+$; 527, 28% $[M - Gly]^+$.

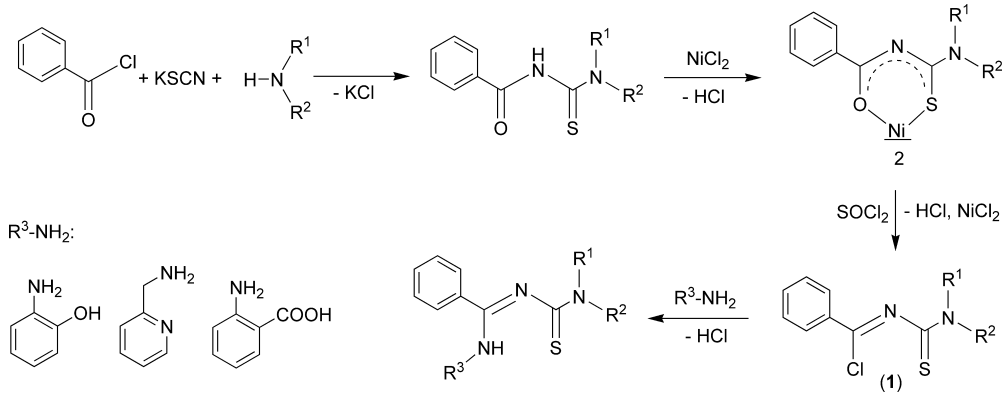
[{ReOCl(L^2)}$_2$O] (8). Method 1. HL^2 (36 mg, 0.11 mmol) in 3 mL of acetone and three drops of NEt_3 were added to a stirred suspension of $[ReOCl_3(PPh_3)_2]$ (83 mg, 0.1 mmol) in 3 mL of CH_2Cl_2. The mixture was heated under reflux for 30 min, whereupon the precursor complex completely dissolved and the color of the reaction mixture changed from yellow-green to violet. The solvent was removed under reduced pressure, and the resulting residue was washed with methanol and recrystallized by slow evaporation of a CH_2Cl_2/acetone solution to yield violet blocklike crystals of **8**.

Method 2. HL^2 (36 mg, 0.11 mmol) was dissolved in 3 mL of acetone and three drops of NEt_3 were added. This solution was added dropwise to a solution of $(NBu_4)[ReOCl_4]$ (58 mg, 0.1 mmol) in 2 mL of acetone. The mixture was stirred at ambient temperature for 2 h and the solvent was removed. The residue was carefully washed with water and extracted with CH_2Cl_2. Recrystallization from CH_2Cl_2/acetone yielded violet crystals. Yield: 91% (52 mg) for method 1, 40% (23 mg) for method 2. Anal. Calcd for $C_{36}H_{42}Cl_2N_8O_3S_2Re_2$: C, 37.85; H, 3.68; N, 9.81; S, 5.61%. Found: C, 37.52; H, 3.44; N, 10.02; S, 5.35%. IR (ν in cm^{-1}): 1488 s (C═N), 949 w (Re═O), 683 s (Re—O—Re). ^1H NMR ($CDCl_3$; δ, ppm): 0.99 (t, $J = 7.0$ Hz, 3 H, CH_3), 1.06 (t, $J = 7.0$ Hz, 3 H, CH_3), 3.19 (m, 1 H, CH_2), 3.39 (m, 1 H, CH_2), 3.95 (m, 1 H, CH_2), 4.03 (m, 1 H, CH_2), 5.03 (d, $J = 19.2$ Hz, 1 H, $PyCH_2$), 5.99 (d, $J = 19.2$ Hz, 1 H, $PyCH_2$), 7.39−7.48 (m, 6 H, Ph), 7.37 (t, $J = 7.4$ Hz, 1 H, Ph), 8.79 (d, $J = 5.6$ Hz, 2 H, Py). ^{13}C NMR ($CDCl_3$; δ, ppm): 48.06 48.70 (N—CH_2), 65.99, 66.51 (O—CH_2), 117.29,

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

	H_2L^3·MeOH	[ReO(L^{1b})Cl]	[TcO(L^{1a})Cl]	[ReO(L^{1a})(Gly)]	[{ReOCl(L^2)}$_2$O]	[ReO(L^3)Cl]$_2$
	4·MeOH	**5b**	**6a**	**7**	**8**	**9**
formula	$C_{20}H_{25}N_3O_3S$	$C_{18}H_{17}ClN_3O_3ReS$	$C_{18}H_{19}ClN_3O_2STc$	$C_{20}H_{23}N_4O_4ReS$	$C_{36}H_{42}Cl_2N_8O_3Re_2S_2$	$C_{38}H_{38}Cl_2N_6O_6Re_2S_2$
mol wt	387.49	577.06	474.87	601.70	1142.20	1182.16
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
a/Å	21.356(2)	10.310(1)	11.406(1)	13.529(1)	10.003(1)	8.865(1)
b/Å	10.809(1)	12.389(1)	12.878(1)	14.421(1)	10.630(1)	13.704(1)
c/Å	18.663(2)	15.295(1)	13.007(1)	10.887(1)	19.441(2)	16.230(1)
α/deg	90	90	90	90	90	90
β/deg	102.37(1)	103.25(1)	93.06(1)	91.11(1)	99.54(1)	90.92(1)
γ/deg	90	90	90	90	90	90
V/Å^3	4208.1(7)	1901.6(3)	1907.8(3)	2123.6(3)	2038.5(3)	1971.4(3)
space group	*C*2/*c*	*P*2$_1$/*n*	*P*2$_1$/*c*	*P*2$_1$/*c*	*P*2$_1$/*n*	*P*2$_1$/*c*
Z	8	4	4	4	2	2
D_{calcd}/g cm^{-3}	1.223	2.016	1.653	1.882	1.861	1.991
μ/mm^{-1}	0.178	6.665	1.022	5.855	6.212	6.431
no. of reflns	14200	16231	9486	12394	7811	14571
no. of independent	5641	5099	5054	4451	4181	5306
no. params	247	244	235	295	241	253
R1/wR2	0.0633/0.1079	0.0475/0.1183	0.0502/0.1219	0.0306/0.0643	0.0341/0.0648	0.0532/0.0940
GOF	1.077	1.089	0.954	1.040	0.949	0.914

Scheme 1



120.50, 124.60, 127.00, 127.63, 128.40, 128.49, 128.92, 131.04, and 134.24 (Ph + Py), 149.45 (C═N), 187.57 (C═S). FAB$^+$ MS (*m*/*z*): 544, 32% [ReO$_2$(L^2)]$^+$; 528, 30% [ReO(L^2)]$^+$.

[ReO(L^3)Cl]$_2$ (9). (NBu_4)[$ReOCl_4$] (58 mg, 0.1 mmol) was added to a solution of H_2L^3 (36 mg, 0.1 mmol) in 5 mL of MeOH. The mixture was stirred at room temperature for 15 min and reduced in volume to about 2 mL. X-ray quality green crystals of **9** deposited from this solution within several days. Yield: 87% (49 mg). Anal. Calcd for $C_{38}H_{38}Cl_2N_6O_6S_2Re_2$: C, 38.60; H, 3.22; N, 7.11; S, 5.42%. Found: C, 38.75; H, 2.98; N, 6.52; S, 5.27%. IR (*ν* in cm^{-1}): 1542 vs, br (C═N, C═O), 1002 s (Re═O). ^{1}H NMR (DMSO; *δ*, ppm): 1.31−1.38 (m, 6 H, CH_3), 3.80−4.20 (m, 4 H, CH_2), 6.51 (d, *J* = 8.1 Hz, 1 H, PhCOO), 6.95 (t, *J* = 8.0 Hz, 1 H, PhCOO), 7.16 (t, *J* = 7.5 Hz, 1 H, PhCOO), 7.34 (m, 3 H, Ph), 7.63 (d, *J* = 8.1 Hz, 1 H, Ph), 8.18 (d, *J* = 8.2 Hz, 2 H, Ph).

X-ray Crystallography. The intensities for the X-ray determinations were collected on a STOE IPDS 2T instrument with Mo Kα radiation (*λ* = 0.71073 Å). Standard procedures were applied for data reduction and absorption correction. Structure solution and refinement were performed with SHELXS97 and SHELXL97.[12] 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.

(12) Sheldrick, G. M. *SHELXS-97 and SHELXL-97, programs for the solution and refinement of crystal structures*; University of Göttingen: Göttingen, Germany, 1997.

Additional information on the structure determinations has been deposited with the Cambridge Crystallographic Data Center.

Results and Discussion

Preparation of the Ligands. *N*-[*N*′,*N*′-Dialkylamino(thiocarbonyl)]benzimidoyl chlorides (**1**) are reactive building blocks, which can readily be prepared by reactions of *N*,*N*-dialkyl-*N*′-benzoylthioureatonickel(II) chelates with $SOCl_2$.[1,2] Modifications of the residues R^1 and R^2 allow for the variation of basic properties of the products such as solubility, polarity, and lipophilicity. Furthermore, the fine-tuning of such properties requires a third molecular position. We have now synthesized the first representatives of a novel class of tridentate *N*-[(*N*″,*N*″-dialkylamino)(thiocarbonyl)]-*N*′-substituted benzamidine ligands by reactions of the appropriate *N*-[*N*′,*N*′-dialkylamino(thiocarbonyl)]benzimidoyl chlorides and functionalized primary amines such as 2-aminophenol, 2-aminomethylpyridine, and 2-aminobenzoic acid in dry acetone (Scheme 1). In the presence of the supporting base NEt_3, such reactions proceed quickly under mild conditions. They can be performed at room temperature as in the case of the preparation of HL^2 or in warm acetone (40 °C) as in the case of the synthesis of HL^1. The progress of the reaction can readily be checked by thin-layer chromatography on alumina and is indicated by the formation of a colorless precipitate of

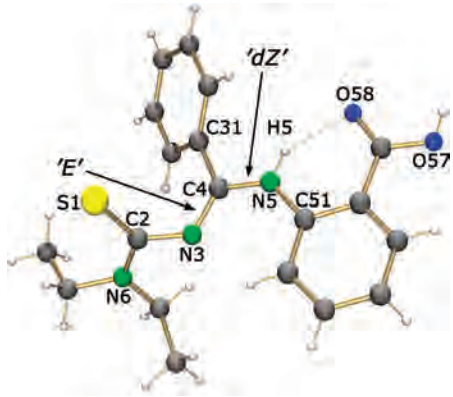


Figure 1. Molecular structure of H_2L^3 (**4**) together with the intramolecular hydrogen bond (N5−H5, 0.86 Å; H5···O58, 1.93 Å; N5···O58, 2.655(3) Å; >N5−H5···O58, 140.8°).

Table 2. Selected Bond Lengths (Å) and Angles (deg) in **4**

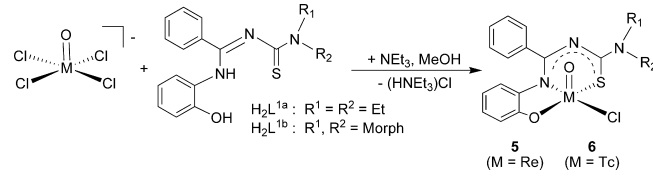
S1−C2	1.678(3)	C4−N5	1.363(4)
C2−N6	1.330(4)	N5−C51	1.402(4)
C2−N3	1.383(4)	C57−O57	1.305(4)
N3−C4	1.290(4)	C57−O58	1.220(4)
C4−C31	1.493(5)		
S1−C2−N3	120.4(3)	C4−N5−C51	130.8(3)
S1−C2−N6	124.0(2)	N5−C51−C56	118.1(3)
C2−N3−C4	123.7(3)	C56−C57−O58	124.6(3)
N3−C4−N5	121.1(3)		

NEt_3·HCl, which is almost insoluble in acetone. The ligands were obtained as crystalline solids in high yields. They were characterized by elemental analysis and spectroscopic methods such as IR, ^{1}H NMR, and ^{13}C NMR.

The ligands H_2L^1 (**2**) and HL^2 (**3**) have good solubility in methanol and acetone. Their ^{1}H NMR spectra are characterized by two sets of well-separated signals corresponding to their alkyl residues, which are due to the hindered rotation around of the C−NEt_2 or C−$N(CH_2)_2O$ bonds. This finding has also been observed with their parent *N*,*N*-dialkylbenzoylthioureas.[13] However, the C−NR^1R^2 bonds of *N*,*N*-dialkylbenzoylthioureas seem to be more flexible, as indicated by broad signals in their ^{1}H NMR spectra.

The synthesis of the anthranilic acid derivative H_2L^3 (**4**) follows the general route described previously for the other dialkylamino(thiocarbonyl)benzamidines. The compound is separated as a yellow oil upon concentration of the reaction mixture. This compound, which is analytically pure H_2L^3 according to IR and NMR spectra, can be crystallized from a concentrated MeOH solution stored in a deep freezer. Slightly yellow crystals of the methanol solvate H_2L^3·MeOH deposit over a period of several days. Figure 1 illustrates the structure of H_2L^3 together with the intramolecular hydrogen bond. Additional hydrogen bonds are established between S1 and O57 and the solvate MeOH molecule. Selected bond lengths and angles are summarized in Table 2. While the C4−N3 bond of 1.290 Å is within the expected range of C=N double bonds, the C4−N5 bond of 1.363 Å has only partial double-bond character. This is found in all similar ligands and suggests that the proton is mainly located at the N5 atom. The configuration of the H_2L^3 molecule is best described as *E*, *dZ*, which has also been found in some related ligands.[3b,7b,17] The *E*, *dZ* configuration is obtained due to the intramolecular hydrogen bond between N5 and O58, which is more stable than a potential hydrogen bonding between N5 and S1.

Complexes of HL^1. Reactions of H_2L^1 with the common rhenium(V) precursor $(NBu_4)[ReOCl_4]$ in methanol at room temperature yield red solids of the composition $[ReOCl(L^1)]$ (**5**) in excellent yields. Corresponding reactions with the less soluble $[ReOCl_3(PPh_3)_2]$ give the same products but with significantly lower yields. This is mainly due to the formation of side products with remaining PPh_3 ligands, which cause difficulties during the isolation of the complexes. The products are sparingly soluble in methanol and acetone and almost insoluble in pentane or hexane. IR spectra of complexes of **5** exhibit strong bands near the 1525 cm^{-1} region but no absorptions in the range between 1612 and 1620 cm^{-1}, where the $\nu_{C=N}$ stretches in the spectra of the noncoordinated benzamidines typically appear.[1] This corresponds to a bathochromic shift of about 100 cm^{-1} and indicates chelate formation with a large degree of π-electron delocalization within the chelate rings. The absence of absorptions in the regions around 3350 cm^{-1} and 3150 cm^{-1}, which correspond to ν_{NH} and ν_{OH}, respectively, in the uncoordinated H_2L^1, indicates the expected double deprotonation of the ligands during complex formation. Intense bands appear between 991 and 995 cm^{-1}, which can be assigned to the Re=O vibrations.[14]



The NMR spectra of complexes of **5** provide additional evidence for the proposed composition and molecular structure of the complexes. The two expected triplet signals of the methyl groups are observed in the ^{1}H NMR spectrum of **5a**. Furthermore, ^{1}H NMR reflects the rigid structure of the tertiary amine nitrogen atom. The appearance of four proton signals of the methylene groups shows that they are magnetically not equivalent with respect to their axial and equatorial positions. This leads to complex coupling patterns in the proton spectra of **5a** and **5b**. ^{13}C NMR spectra of complexes **5a** and **5b** exhibit a pattern similar to the spectra of the noncoordinated ligands, in which a couple of signals for the CH_2 and CH_3 groups appears in each. Deprotonation of the aromatic C_{ar}−NH and C_{ar}−OH groups during the complex formation of the H_2L^1 ligands results in a strong shift from their respective ^{13}C NMR chemical shifts of 145 ppm and 165 ppm.

Figure 2 depicts the molecular structure of compound **5b** as a prototype compound for this type of complexes.

(13) (a) Fitzl, G.; Beyer, L.; Sieler, J.; Richter, R.; Kaiser, J.; Hoyer, E. *Z. Anorg. Allg. Chem.* **1977**, *433*, 237. (b) Irving, A.; Koch, K. R.; Matoetoe, M. *Inorg. Chim. Acta* **1993**, *206*, 193. (c) Sacht, C.; Datt, M. S.; Otto, S.; Roodt, A. *J. Chem. Soc., Dalton Trans.* **2000**, 727.

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

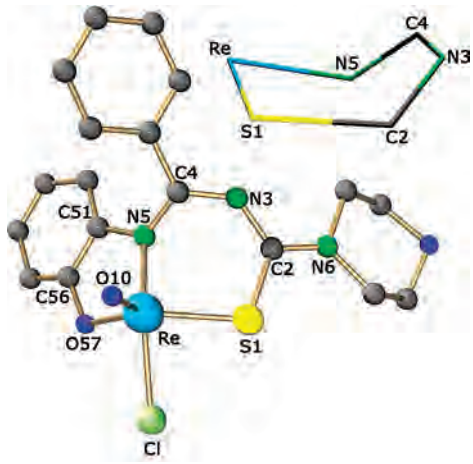


Figure 2. Molecular structure of [ReOCl(L[1b])] (**5b**) and a perspective view of the six-membered chelate ring. H atoms have been omitted for clarity.

Table 3. Selected Bond Lengths (Å) and Angles (deg) in **5b** and **6a**

	5b M=Re	**6a** M=Tc		**5b** M=Re	**6a** M=Tc
M−O10	1.665(7)	1.642(6)	C2−N3	1.33(1)	1.347(9)
M−Cl	2.344(2)	2.351(2)	N3−C4	1.31(1)	1.304(8)
M−S1	2.289(2)	2.296(2)	C4−N5	1.37(1)	1.386(8)
M−N5	1.999(7)	1.991(5)	N5−C51	1.42(1)	1.435(7)
M−O57	1.957(6)	1.994(4)	C56−O57	1.35(1)	1.374(9)
S1−C2	1.786(9)	1.758(8)	C2−N6	1.33(1)	1.321(9)
O10−M−Cl	104.4(3)	106.1(2)	C2−N3−C4	127.5(8)	126.1(6)
O10−M−S1	108.6(3)	111.2(2)	N3−C4−N5	123.8(8)	124.0(6)
O10−M−N5	106.1(3)	104.8(2)	C4−N5−M	117.4(5)	118.1(4)
O10−M−O57	114.8(3)	114.0(2)	C4−N5−C51	125.0(7)	123.4(5)
M−S1−C2	106.7(3)	106.6(2)	N5−C51−C56	111.6(7)	109.2(6)
S1−C2−N3	121.9(7)	123.5(5)	C56−O57−M	116.7(5)	115.5(4)
S1−C2−N6	118.6(7)	119.0(5)			

Selected bond lengths and angles are given in Table 3. The rhenium atom exhibits a distorted square-pyramidal environment with the oxo ligand in the apical position. The square plane defined by the donor atoms of the tridentate ligand and the chloro ligand is slightly distorted, with a main distortion of 0.124(3) Å from a mean least-squares plane for atom O57. The Re atom is situated by 0.537 Å above this plane toward the oxo ligand. All O10−Re−X angles (X = equatorial donor atom) fall in the range between 104 and 114°. This corresponds with the typical bonding situation of square-pyramidal $Re^{V}O$ complexes.[15] The Re=O distance of 1.665(7) Å is within the expected range of a rhenium−oxygen double bond.[14] Despite the fact that the six-membered chelate ring is not planar (see also the wireframe model of the chelate ring in Figure 2), a considerable delocalization of π-electron density is indicated by the observed bond lengths. The C−S and C−N bonds inside the chelate ring fall within the range between carbon−sulfur and carbon−nitrogen single and double bonds. This bond length equalization is even extended to the C2−N6 bond of 1.330(4) Å, which is significantly shorter than expected for a single bond. The partial transfer of electron density into this bond

(15) (a) Hansen, L.; Xu, X.; Lipowska, M.; Taylor, A, Jr.; Marzilli, L. G. *Inorg. Chem.* **1999**, *38*, 2890. (b) O'Neil, J. P.; Wilson, S. R.; Katzenellenbogen, J. A. *Inorg. Chem.* **1994**, *33*, 319.

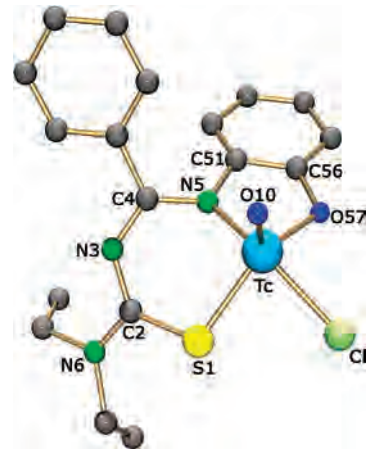


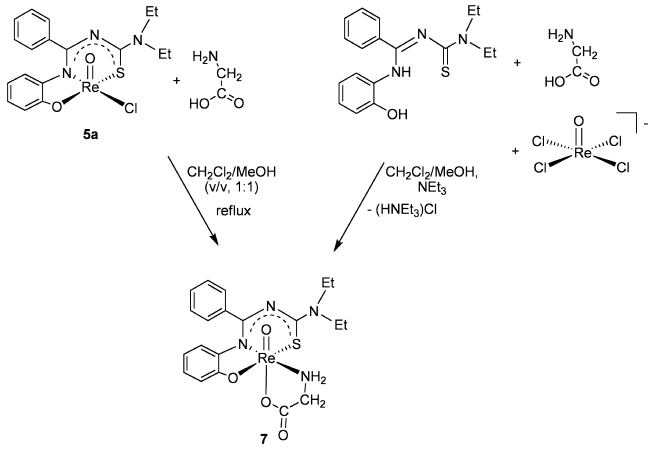
Figure 3. Molecular structure of [TcOCl(L[1a])] (**6a**). H atoms have been omitted for clarity.

strongly agrees with the ^{1}H NMR spectrum of the compound, which indicates a rigid arrangement of the morpholine ring in the complex.

An analogous technetium complex was prepared by the reaction of $(NBu_4)[TcOCl_4]$ with H_2L^{1a} in methanol. The reaction was performed at room temperature, and a red, crystalline product of the composition [TcOCl(L[1a])] (**6a**) precipitated directly from the reaction mixture in good yields. The IR spectrum of **6a** exhibits a $\nu_{(Tc=O)}$ frequency at 972 cm^{-1} and indicates a strong bathochromic shift of the C=N band, as a consequence of the complex formation. The ^{1}H NMR spectral features previously described for **5a** also apply to the Tc compound. The same holds true for the main structural features of the solid-state structures of the compounds. Figure 3 depicts the molecular structure of **6a**, and the corresponding bond lengths are compared to those of **5b** in Table 3. As discussed for the rhenium compound, the Tc atom has a distorted square-pyramidal geometry and is located 0.552 Å above the basal plane formed by S1, N5, O57, and Cl. The Tc−O10 distance of 1.642 Å is within the typical Tc−O double bond range.

The chloro ligands in the coordination spheres of the compounds of **5** and complex **6a** are sufficiently labile to allow further ligand exchange. Thus, the reaction of **5a** with glycine, Hgly, in a CH_2Cl_2/MeOH mixture yields the dark red mixed-ligand complex [ReO(L[1a])(gly)] (**7**) in good yields. The same product is formed in a one-pot reaction starting from $(NBu_4)[ReOCl_4]$ and 1 equiv of HL^{1a} in a CH_2Cl_2/MeOH mixture followed by the addition of a slight excess of Hgly.

In both cases, the addition of a base such as NEt_3 supports the deprotonation of glycine. The IR spectrum of **7** shows a medium broad band at 3425 cm^{-1} and a strong absorption at 1651 cm^{-1}, which can be assigned to ν_{NH} and ν_{CO} stretches of the chelating glycinate ligand. While the absorption of the Re=O vibration shifts to longer wavelengths by about 20 cm^{-1} with respect to **5a**, the absorption of the C=N stretch moves to the shorter wave region by about 15 cm^{-1}. The chelate formation of the glycinate ligand is indicated by the detection of magnetically unequal protons of methylene and amino groups in the NMR spectrum of the compound. Thus, two multiplet signals for each proton of the CH_2 group are



observed due to the combination of the geminal coupling and the vicinal coupling with the adjacent NH_2 group. One of them is well resolved at 3.50 ppm, and the other is partially covered by the NCH_2 signals of the L^{1a} ligand in the range between 3.9 and 4.1 ppm. Two broad signals of the NH_2 protons appear at 5.87 ppm and 6.85 ppm.

The molecular structure of **7** is depicted in Figure 4. This structure confirms the results of the spectroscopic studies. The rhenium atom is placed in a distorted octahedral coordination environment, which is formed by the oxo oxygen, an equatorially coordinated $(L^{1a})^{2-}$ ligand and a bidentate glycinate. The amino group occupies the remaining equatorial position, whereas the carboxylate group coordinates trans to the oxo ligand. With respect to the structure of the five-coordinate **5a**, the rhenium atom expectedly drops toward the equatorial plane. While the Re−O10 distance is slightly lengthened, all C−N and C−S bonds in the chelate ring are slightly shortened. This is in agreement with the IR spectroscopic results. Nevertheless, the Re−O10 bond length of 1.680 Å falls into the typical range of Re═O double bonds. The Re−N11 (2.189 Å) and Re−O15 (2.120 Å) bond lengths are about 0.1 Å longer than the Re−N5 and Re−O57 bonds, which reflects the coordination of the NH_2 group as an amine and the trans influence of the oxo ligand. Selected bond lengths and angles of **7** are given in Table 4.

Complex Formation with HL^2. Treatment of $[ReOCl_3(PPh_3)_2]$ with HL^2 in CH_2Cl_2/acetone at room temperature results in the immediate formation of a green solution, which slowly changes to a brown color when an alcohol is added. Up until now, each of our attempts to isolate crystalline products from such solutions failed. However, the green color of the solution described above immediately turns to violet after the addition of a base such as NEt_3. From this solution, the crystalline violet complex $[\{ReOCl(L^2)\}_2O]$ **8** was isolated in high yield. The same compound can be prepared from $(NBu_4)[ReOCl_4]$ but with lower yields. The formation of an oxo-bridged dimer is not unexpected with this monoanionic, tridentate ligand and is frequently observed when traces of water are present. Furthermore, charge compensation more favorably allows for the formation of a neutral dimeric rhenium−oxo complex rather than a complex cation.[14]

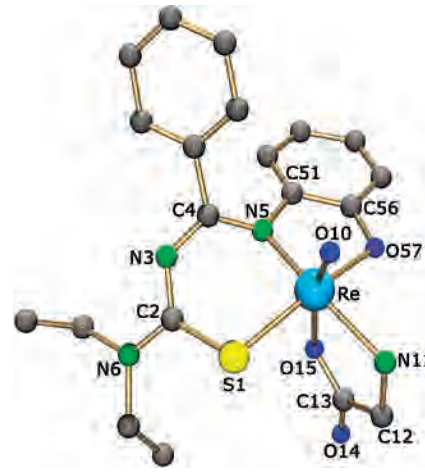
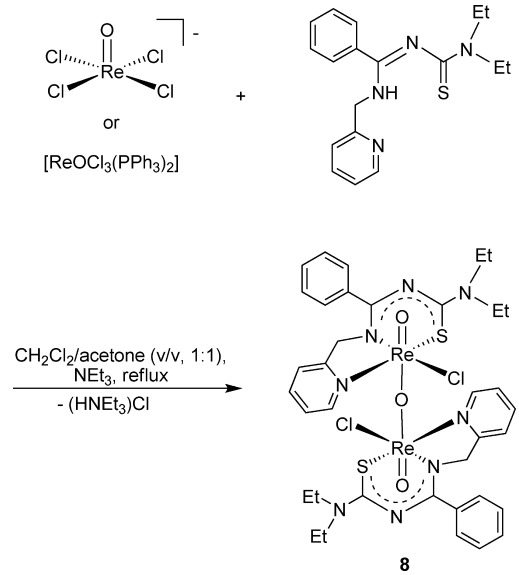


Figure 4. Molecular structure of $[ReO(L^{1a})(gly)]$ (**7**). H atoms have been omitted for clarity.

Table 4. Selected Bond Lengths (Å) and Angles (deg) in **7**

Re−O10	1.680(5)	C4−N5	1.353(8)
Re−S1	2.348(2)	C2−N6	1.328(9)
Re−N5	1.989(5)	N5−C51	1.419(8)
Re−O57	2.029(5)	C56−O57	1.354(8)
Re−N11	2.189(6)	N11−C12	1.46(1)
Re−O15	2.120(5)	C12−C13	1.52(1)
S1−C2	1.760(7)	C13−O14	1.210(9)
C2−N3	1.330(9)	C13−O15	1.300(8)
N3−C4	1.304(8)		
O10−Re−S1	98.4(2)	N3−C4−N5	124.8(6)
O10−Re−N5	104.7(2)	C4−N5−C51	122.4(5)
O10−Re−O57	100.3(2)	N5−C51−C56	113.4(6)
O10−Re−N11	90.5(2)	C51−C56−O57	117.6(6)
O10−Re−O15	164.6(2)	C56−O57−Re	113.2(4)
Re−S1−C2	103.5(2)	Re−N11−C12	114.6(4)
S1−C2−N3	123.3(5)	N11−C12−C13	112.0(6)
S1−C2−N6	119.6(5)	C12−C13−O15	113.5(6)
C2−N3−C4	127.6(6)	C13−O15−Re	123.5(4)



The IR spectrum of **8** exhibits a strong bathochromic shift of the C═N vibration of about 120 cm^{-1} and the absence of the medium broad N−H stretch band at 3217 cm^{-1}, with respect to the IR spectrum of the uncoordinated HL^2. Moreover, the formation of an oxo-bridged dimeric compound is strongly indicated by a weak absorption of the Re═O stretch at 949 cm^{-1} and a strong absorption of the

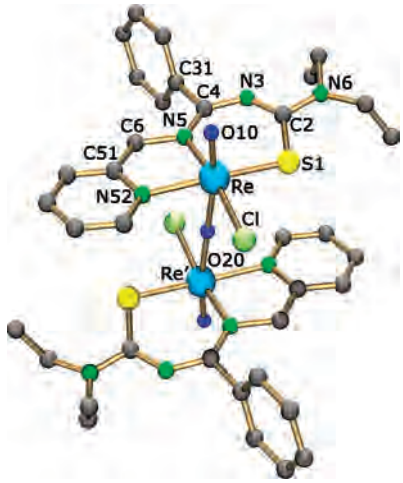


Figure 5. Molecular structure of $[\{ReOCl(L^2)\}_2O]$ (**8**). H atoms have been omitted for clarity.

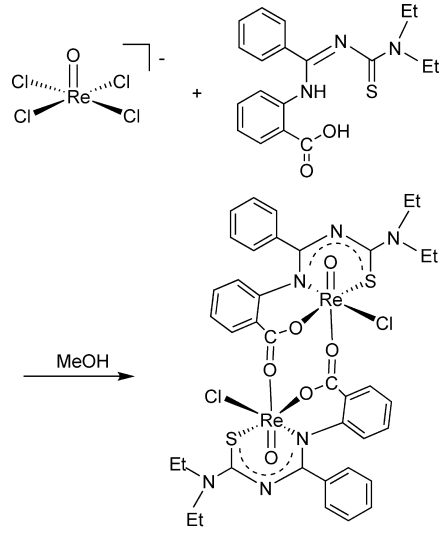
Re—O—Re′ unit at 683 cm^{-1}.[16] In the ^1H NMR spectrum of **8**, the protons of the ethyl residues show similar patterns as those observed in **5a**. As expected, the two methylene protons at C6 of the $(L^2)^-$ ligand are magnetically nonequivalent. FAB^+ mass spectra show no evidence of the molecular ion peak. Preferably, the Re—O—Re bond is cleaved as evidenced by peaks corresponding to the $[ReO_2(L^2)]^+$ (m/z = 544) and/or $[ReO(L^2)]^+$ (m/z = 528) fragments.

X-ray quality single crystals of **8** were obtained by the slow evaporation of a CH_2Cl_2/acetone solution. Figure 5 depicts the molecular structure of **8**, showing a dimer with O20 as a center of inversion. The coordination sphere of the metal atom is best described as a slightly distorted octahedron with trans angles between 168.9(1) and 172.1(1)°. The tridentate organic ligand is singly deprotonated and coordinates equatorially to the Re center. The established six-membered and five-membered chelate rings are almost planar and show a maximum deviation from planarity for atom S1 (0.182 Å). The Re atom is only slightly (0.098 Å) shifted out of the mean least-squares plane, which is formed by the atoms S1, N5, N52, and Cl. The described coordination mode leaves less space for an "in-plane" arrangement of the phenyl ring. Consequently, the plane of this ring stands almost perpendicular to the plane of the adjacent chelate ring, and conjugation of π-electron density between these rings is prevented, as can be seen in the relatively long C4—C31 bond length of 1.502(8) Å. Additional bond lengths and angles of **8** are given in Table 5.

Complex Formation with H_2L^3. The reaction of $(NBu_4)[ReOCl_4]$ with an equivalent amount of H_2L^3 in methanol results in ligand exchange and the formation of an oxorhenium(V) complex of the composition $[ReOCl(L^3)]_2$ (**9**), which can be isolated as a green, microcrystalline solid directly from the reaction mixture.

Table 5. Selected Bond Lengths (Å) and Angles (deg) in **8**

Re—O10	1.692(4)	N3—C4	1.336(8)
Re—N52	2.156(5)	C4—N5	1.329(7)
Re—N5	2.038(5)	C2—N6	1.352(8)
Re—S1	2.332(2)	N5—C6	1.485(8)
Re—Cl	2.458(2)	C6—C51	1.502(8)
Re—O20	1.916(3)	C51—N52	1.345(9)
S1—C2	1.745(6)	C4—C31	1.502(8)
C2—N3	1.325(9)		
O10—Re—N52	88.3(2)	N52—Re—Cl	93.9(2)
O10—Re—N5	94.7(2)	N52—Re—S1	172.1(1)
O10—Re—S1	98.2(2)	N5—Re—Cl	171.5(2)
O10—Re—Cl	91.0(2)	O20—Re—N52	81.1(1)
O10—Re—O20	168.9(1)	O20—Re—N5	86.8(2)
N52—Re—N5	80.0(2)	O20—Re—S1	92.64(4)
N5—Re—S1	94.84(14)	O20—Re—Cl	86.36(4)
S1—Re—Cl	90.59(5)		



9

The IR spectrum of **9** shows the disappearance of a broad band at 3163 cm^{-1} of the O—H vibration of **4** and a very strong shift of the C=O stretch from 1683 cm^{-1} in the uncoordinated H_2L^3 to 1542 cm^{-1} in the complex. This is commonly observed when carboxylato ligands coordinate to metal centers via both oxygen atoms.[18] A strong band at 1002 cm^{-1} is assigned as the Re=O stretching band. The poor solubility of **9** in organic solvents, even in DMSO, causes difficulties in the elucidation of its structure by spectroscopic methods. The ^1H NMR spectrum of **9** in DMSO-d_6 is less intense, and the signals are not sufficiently resolved to allow a detailed analysis of the coupling patterns. Nevertheless, all protons of the ligand can be assigned and integrated in the required ratio. Green blocks of **9** are stable in the air and could be studied by X-ray diffraction without noticeable decomposition. Figure 6 illustrates the dimeric structure of the compound. Selected bond lengths and angles are summarized in Table 6. Each of the organic ligands establishes a tridentate equatorial coordination at one ReO unit. The remaining

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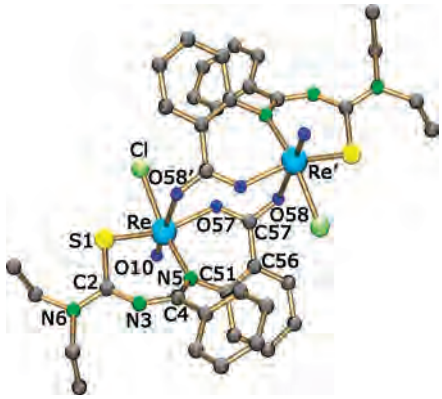


Figure 6. Molecular structure of [{ReOCl(L^3)}$_2$] (**9**). H atoms have been omitted for clarity.

Table 6. Selected Bond Lengths (Å) and Angles (deg) in **9**[a]

Re−O10	1.655(8)	C2−N3	1.34(1)
Re−Cl	2.376(3)	C2−N6	1.33(1)
Re−S1	2.295(3)	N3−C4	1.33(1)
Re−N5	2.040(8)	C4−N5	1.34(1)
Re−O57	2.051(7)	N5−C51	1.44(1)
Re−O58′	2.271(7)	C57−O57	1.28(1)
S1−C2	1.75(1)	C57−O58	1.25(1)
O10−Re−Cl	96.4(3)	C2−N3−C4	130.9(9)
O10−Re−S1	101.6(3)	N3−C4−N5	125.1(9)
O10−Re−N5	97.4(4)	C4−N5−C51	117.6(9)
O10−Re−O57	88.5(3)	N5−C51−C56	124.0(9)
O10−Re−O58′	175.8(3)	C56−C57−O58	120.0(9)
S1−C2−N3	124.3(9)	C57−C58−Re′	122.1(6)
S1−C2−N6	118.2(9)	C4−N5−C51	117.6(9)

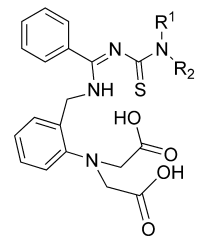
[a] Symmetry operation: (′) $-x$, $1-y$, $-z$.

position in the basal plane of the resulting square pyramid is occupied by a chloro ligand. Dimerization is achieved by coordination of the oxygen atom O58 of a second {ReO(L^3)Cl} unit trans to the oxo oxygen. Thus, each of the rhenium atoms has a distorted octahedral environment, and the resulting dimeric molecule possesses inversion symmetry. The Re···Re′ distance is 5.324 Å, and binding interactions between the metal atoms can be excluded. To the best of our knowledge, such a bridging coordination of a carboxylic group in a rhenium complex with the transition metal in one of its high oxidation states is without precedent. Most of the hitherto structurally characterized rhenium complexes with bridging carboxylate coordination establish metal−metal bonds[19] or contain the tricarbonylrhenium(I) core.[20]

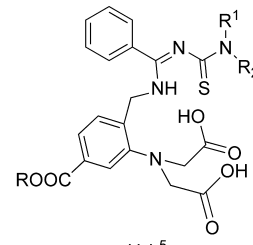
Conclusions

The tridentate benzamidines described above are the first representatives of a novel, versatile class of ligands, which are well suited for the formation of stable complexes with rhenium(V) and technetium(V) centers. Substitutions in their periphery allow for the control of the coordination mode of the metal. The stability of the complexes and the high synthetic potential of benzamidine ligands justify the use of this new class of compounds in further experiments, particularly, such as the synthesis of bioconjugates with ^{99m}Tc or ^{186,188}Re. Of particular interest, the monomeric complexes of **5** may be adopted for a mixed-ligand (3 + 2 or 3 + 1 + 1) radiopharmaceutical design.

When designing radioactive bioconjugates using this new class of compounds, a more generalized route for the synthesis of the ligands described in this communication is advisable: it can easily be extended to amines with three or four additional potential donor atoms.



H_3L^4



H_3L^5

Such multidentate ligand systems can be readily attached to an anchor group for couplings with peptides or proteins. Corresponding experiments (e.g., with the multidentate benzamidines H_3L^4 and with bioconjugatable derivatives such as H_3L^5) are being performed in our laboratory.

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Supporting Information Available: X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC702344S

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