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Rhenium(I) tris(carbonyl) complexes with soft scorpionates

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The novel tris(mercaptoimidazolyl)borate ligands Li[RB(tim^{Me})$_3$] (R = Me (**1**), Ph (**2**)) have been synthesized by reaction, in refluxing toluene, of 2-mercapto-1-methylimidazole with lithium methylborohydride or phenylborohydride, respectively. By reacting **1** and **2** with the Re(I) starting material $(NEt_4)_2[Re(CO)_3Br_3]$, the tris(carbonyl) complexes [Re{RB(tim^{Me})$_3$-κ^3*S*,*S*,*S*}(CO)$_3$] (R = Me (**3**), Ph (**4**)) have been obtained in moderate yields. Compounds **1**–**4** have been characterized by IR, ^{1}H, and ^{11}B NMR spectroscopies, and also by X-ray crystallographic analysis in the case of **3**. The X-ray diffraction analysis of **3** showed that the rhenium atom adopts a slightly distorted octahedral coordination with a facial arrangement of the carbonyl ligands. The three remaining coordination positions are occupied by the thione sulfur atoms from the tripodal methyltris(2-mercapto-1-methylimidazolyl)borate, which adopts a typical propeller-like configuration.

Introduction

Recent studies on the basic coordination chemistry of Tc(I) and Re(I) complexes containing the *fac*-M(CO)$_3$ moieties highlighted the potential relevance of these complexes in the development of radioactive products for diagnostic (^{99m}Tc) and therapeutic ($^{186/188}$Re) medical applications.[1–14] Searching for novel Tc(I) and Re(I) tris(carbonyl) complexes useful for biomedical applications, our group focused on poly(mercaptoimidazolyl)borates as ancillary ligands.[15] Several Re and ^{99m}Tc complexes have been prepared in high yield and with high specific activity,[15,16] showing that poly(mercaptoimidazoyl)-borates feature inherent requirements for their application in the radiopharmaceutical field. Most relevantly, poly(mercaptoimidazolyl)borates can be easily modified by the controlled introduction of different substituents, allowing a fine tuning of the physico-chemical properties of the complexes, such as size or lipophilicity. In radiopharmaceutical research, this tuning is a crucial issue, as these properties strongly influence the transport of the complexes inside the body, namely their ability to cross biological membranes.[17]

Following our efforts to modify poly(mercaptoimidazolyl)-borates for further application in radiopharmaceutical development,[15] we started to evaluate the possibility of preparing tris(mercaptoimidazolyl)borates featuring alkyl or aryl groups directly attached to the boron atom.

Herein, we report on the synthesis and characterization of the novel Li[RB(tim^{Me})$_3$] (R = Me (**1**), Ph (**2**)) and on their reactions with the Re(I) starting material $(NEt_4)_2[ReBr_3(CO)_3]$, which led to the synthesis of the new complexes [Re{RB(tim^{Me})$_3$-κ^3*S*,*S*,*S*}(CO)$_3$] (R = Me (**3**), Ph (**4**)) also described in this work.

Experimental

The synthesis of the tris(mercaptoimidazolyl)borates were performed under a nitrogen atmosphere, using standard Schlenk techniques and dry toluene, while the synthesis of the Re complexes were carried out under air. The starting material $(NEt_4)_2[ReBr_3(CO)_3]$[18] and the organoborohydrides Li(RBH$_3$) (R = Me, Ph)[19] were prepared by literature methods. The other chemicals were used as purchased.

^{1}H and ^{11}B NMR spectra were recorded on a Varian Unity 300 MHz spectrometer; ^{1}H chemical shifts were referenced with the residual solvent resonances relative to tetramethylsilane, and the ^{11}B NMR chemical shifts with an external $NaBH_4$ solution. NMR spectra were run in CD_3CN. IR spectra were recorded as KBr pellets on a Perkin-Elmer 577 spectrometer. Carbon, hydrogen and nitrogen analysis were performed on a EA110 CE Instruments automatic analyser.

Synthesis of Li[RB(tim^{Me})$_3$] (R = Me (1), Ph (2))

To a suspension of Li(RBH$_3$) (R = Me, Ph) in toluene (20 ml) were added three equivalents of solid 2-mercapto-1-methylimidazole, and the resulting mixtures were refluxed for 2 h (R = Me) or 5 h (R =Ph). After cooling to room temperature, ligands **1** and **2** precipitate as white solids, which were recovered by filtration. Further purification of **1** was performed by recrystallization from a concentrated THF solution, followed by washing of the white precipitate with chloroform. The purification of **2** involved just washing with chloroform, to remove any unreacted 2-mercaptoimidazole. Starting from 100 mg of Li(MeBH$_3$) (2.79 mmol) and from 200 mg (2.05 mmol) of Li[PhBH$_3$] were obtained 620 mg of **1** (Yield: 60%) and 318 mg of **2** (Yield = 60%), respectively.

Compound 1. IR (cm^{-1}): 725 (ν(C=S)). ^{1}H NMR (300 MHz, CD_3CN, δ (ppm)): 1.01 (3H, s, CH_3B), 3.42 (9H, s, CH_3N), 6.35 (3H, d, J_{H-H} = 2.1 Hz, CH), 6.63 (3H, d, J_{H-H} = 2.1 Hz, CH). ^{11}B NMR (96 MHz, CD_3CN, δ (ppm)): 44.5.

Compound 2. IR (cm^{-1}): 730 m (ν(C=S)). ^{1}H NMR (300 MHz, CD_3CN, δ (ppm)): 3.41 (9H, s, CH_3N), 6.61 (3H, d, J_{H-H} = 2.1 Hz, CH), 6.80 (3H, br, CH), 7.01 (2H + 1H, m, Ph), 7.20 (2H, br m, Ph). ^{11}B NMR (96 MHz, CD_3CN, δ (ppm)): 44.0.

Synthesis of [Re{RB(tim^{Me})$_3$-κ^3*S*,*S*,*S*}(CO)$_3$] (R = Me (3), Ph (4))

To solutions of $(NEt_4)_2[ReBr_3(CO)_3]$ (100 mg, 0.246 mmol) in methanol were added Li[RB(tim^{Me})$_3$] (R = Me (**1**), Ph(**2**)) in approximate 10% molar excess, and the mixtures were stirred for 1 h at room temperature. Compound **3** and **4** precipitate from the respective reaction mixtures, and were recovered by filtration. After drying under vacuum, compounds **3** (82 mg, yield = 57%) and **4** (68 mg, yield = 40%) were obtained as white microcrystalline solids.

Compound 3. Anal. Calc. for $C_{16}H_{18}N_6O_3S_3BRe$: C, 30.23; H, 2.83; N, 13.23%. Found: C, 30.49; H, 2.19; N, 13.11%. IR (cm^{-1}): 1895s (ν(C–O)), 1860s (ν(C–O)), 732 m (ν(C=S)). ^{1}H NMR (300 MHz, CD_3CN, δ (ppm)): 0.70 (3H, s, CH_3B), 3.61 (9H, s, CH_3N), 6.96 (3H, d, J_{H-H} = 2.4 Hz, CH), 7.03 (3H, br s, CH). ^{11}B NMR (96 MHz, CD_3CN, δ (ppm)): 42.8.

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Table 1 Crystallographic data for **3**

Formula	$C_{16}H_{18}BN_6O_3ReS_3.OC_4H_8$
M/g mol^{-1}	707.66
Crystal system	Triclinic
Space group	$P\bar{1}$ (no. 2)
a/Å	14.053(3)
b/Å	15.030(3)
c/Å	15.128(3)
α/°	74.08(2)
β/°	68.28(2)
γ/°	63.49(1)
V (Å^3)	2633.3(9)
Z	4
D_c/g cm^{-3}	1.785
μ(Mo-Kα)/cm^{-1}	4.891
Reflections collected	9584
Independent reflections	9199 (R_{int} = 0.0454)
Parameters	581
$\Delta\rho$/e Å^{-3}	0.782 and −0.745
Goodness-of-fit	1.066
R^a	0.0592 (0.1222)^b
$wR_2{}^a$	0.0908 (0.1302)^b

^{a} $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma(w(F_o^2 - F_c^2)^2)/[\Sigma(w(F_o^2)^2)]^{1/2}$ [$F_o > 4\sigma(F_o)$]. ^{b} Based on all data.

Compound 4. Anal. Calc. for $C_{21}H_{20}N_6BO_3S_3Re$: C, 36.15; H, 2.87; N, 12.05%. Found: C, 36.03; H, 1.78; N, 11.34%. IR (cm^{-1}): 1895s (ν(C–O)), 1865s (ν(C–O)), 735 (ν(C=S)). ^{1}H NMR (300 MHz, CD_3CN, δ (ppm)): 3.56 (9H, s, CH_3N), 6.88 (3H, d, J_{H-H} = 2.1 Hz, CH), 6.99 (3H, d, J_{H-H} = 2.1 Hz, CH) 7.34 (2H, m, Ph), 7.64 (3H, m, Ph). ^{11}B NMR (96 MHz, CD_3CN, δ (ppm)): 43.5.

X-Ray crystallographic analysis

The crystals of compound **3** were obtained by recrystallization from tetrahydrofuran–*n*-hexane and mounted in thin-walled glass capillaries. Data were collected at room temperature on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo-Kα radiation, using an ω–2θ scan mode. The crystal data are summarized in Table 1.

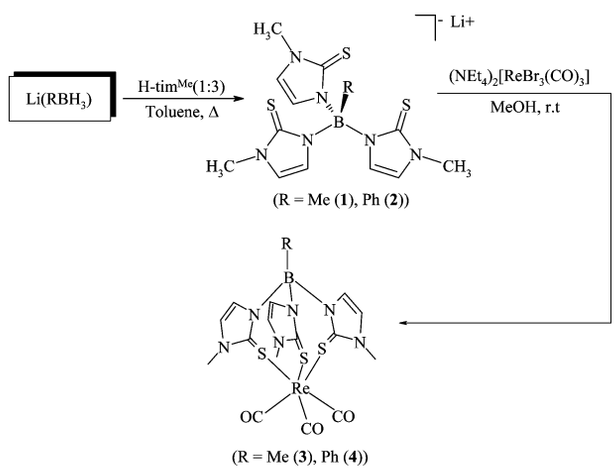
The data were corrected[20] for Lorentz and polarization effects, for linear decay and empirically for absorption by Ψ scans. The heavy atom positions were located by Patterson methods using SHELXS-86.[21] The remaining atoms were located in successive Fourier-difference maps and refined by least-squares refinements on F^2 using SHELXL-93.[22] Complex **3** crystallizes with two independent molecules in the asymmetric unit, and with one molecule of THF of crystallization per formula unit. All the non-hydrogen atoms were refined anisotropically, with the exception of those from the THF of crystallization; the contributions of the hydrogen atoms were included in calculated positions, constrained to ride on their carbon atoms. Geometrical restraints were applied to one of the THF solvent molecules which is severely disordered. Atomic scattering factors and anomalous dispersion terms were as in SHELXL-93.[22] The drawings were made with ORTEP-3;[23] all the calculations were performed on a Dec α 3000 computer.

CCDC reference number 205976.

See http://www.rsc.org/suppdata/dt/b3/b302899b/ for crystallographic data in CIF or other electronic format.

Results and discussion

There are available different synthetic approaches for the preparation of tris(azolyl)borates containing alkyl or aryl substituents directly attached to the boron atom, depending essentially on the boronated starting material. In the case of the ubiquitous pyrazolyl derivatives, alkyl- or aryl-tris(pyrazolyl)-borates have been successfully prepared starting from boronic acids, boronic esters, dihaloboranes or borohydrides.[24] The use of alkyl- or aryl-boronic acids for the synthesis of tris(azolyl)-borates can be quite convenient, as some of these acids are commercially available and easily derivatised with selected biomolecules. However, the need of high temperatures is a potential drawback, which limits the usefulness of boronic acids in the synthesis of thermally unstable poly(azolyl)borates. Being aware that 1-methyl-2-mercaptoimidazole derivatives have a tendency to decompose at high temperatures,[25] we discarded boronic acids as starting materials for the synthesis of alkyl- or aryl- tris(mercaptoimidazolyl)borates. Instead, we focused on alkyl or arylborohydrides, which we had already used for the preparation of $[R(H)B(tim^{Me})_2]^-$ (R = Me, Ph). These bis(mercaptoimidazolyl)borates) are prepared efficiently by reflux of the desired organoborohydrides ($Li[RBH_3]$ = Me, Ph) and 1-methyl-2-mercaptoimidazole, in tetrahydrofuran and with an approximate 1 : 2 molar ratio.[15] We have also explored this approach in the synthesis of the corresponding tris-(mercaptoimidazolyl)borates, using the same solvent but with an increased concentration of 1-methyl-2-mercaptoimidazole (1 : 3 molar ratio). However, even after prolonged reflux in THF (24 h), the bis derivatives were the only products formed. By changing the solvent to toluene, we succeeded in the synthesis of the novel $Li[RB(tim^{Me})_3]$ (R = Me (**1**), Ph (**2**)), which were obtained after refluxing for 2 and 5 h, respectively (Scheme 1).



Scheme 1

The formation of **1** and **2** is quite efficient, as shown by the follow-up of the reactions by ^{1}H and ^{11}B NMR analysis. However, after work-up, compounds **1** and **2** were obtained only in moderate isolated yield, since successive recrystallizations are required to remove any traces of unreacted 2-mercapto-1-methylimidazole. Ligands **1** and **2** are hygroscopic white solids, which are soluble in most common polar organic solvents and in water, and are relatively resistant towards aerobic oxidation and hydrolysis.

As indicated in Scheme 1, treatment of $(NEt_4)_2[Re(CO)_3Br_3]$ with stoichiometric amounts of $Li[RB(tim^{Me})_3]$ (R = Me (**1**), Ph (**2**)), in methanol solution and at room temperature, leads promptly to the novel tris(carbonyl) complexes $[Re\{RB(tim^{Me})_3\text{-}\kappa^3S,S,S\}(CO)_3]$ (R = Me (**3**), Ph (**4**)). Complexes **3** and **4** precipitated upon concentration of the respective reaction mixtures, and were recovered as white microcrystalline solids in moderate yields (40–50%).

$[Re\{RB(tim^{Me})_3\text{-}\kappa^3S,S,S\}(CO)_3]$ (R = Me (**3**), Ph (**4**)) are air- and water-stable compounds, as observed for the analogous $[Re\{HB(tim^{Me})_3\text{-}\kappa^3S,S,S\}(CO)_3]$.[15] However, the attachment of methyl or phenyl groups to the boron atom has a dramatic influence on the solubility of complexes **3** and **4** which are soluble in most common polar organic solvents, in contrast to $[Re\{HB(tim^{Me})_3\text{-}\kappa^3S,S,S\}(CO)_3]$. These findings clearly show that the introduction of different substituents in poly-(mercaptoimidazolylborates modulates the physico-chemical properties of the corresponding rhenium tris(carbonyl)

complexes, what is quite relevant for their potential application in radiopharmaceutical development.

The ligands, **1** and **2**, and the respective complexes, **3** and **4**, have been characterized by C, H, N analysis, IR, ^{1}H, and ^{11}B NMR spectroscopies, and also by X-ray crystallographic analysis in the case of **3**. For ligands **1** and **2**, it was not possible to obtain accurate elemental analysis, although ^{1}H and ^{11}B NMR spectroscopies indicated that we obtained pure samples.

The IR spectra of Li[RB(tim^{Me})$_3$] (R = Me (**1**), Ph (**2**)) present medium intense bands centered at around 730 cm^{-1}, which were attributed to ν(C=S). The frequencies of these bands are almost insensitive to the coordination of the ligands to the *fac*-[Re(CO)$_3$]$^+$ moiety and appear at 732 and 735 cm^{-1} for **3** and **4**, respectively. This kind of behaviour has been already observed for several coordination complexes with poly(mercaptoimidazolyl)borates.[25–43] The IR spectra of compounds [Re{RB(tim^{Me})$_3$-κ^3*S*,*S*,*S*}(CO)$_3$] (R = Me (**3**), Ph (**4**)) display two strong bands due to the ν(CO) stretching mode, in the range 1860–1895 cm^{-1} and with the typical pattern observed for complexes with the "*fac*-Re(CO)$_3$" moiety in a C_3 environment.[15]

The ^{1}H NMR spectra of complexes **3** and **4** are quite simple, showing two doublets for the methyne protons of the mercaptoimidazolyl rings and one singlet for the N–CH$_3$ group of the same rings, in a 3 : 3 : 9 ratio. This pattern is consistent with the chemical and magnetic equivalence of the coordinated rings, in accordance with the expected C_3 symmetry. The ^{1}H NMR spectrum of ligand Li[PhB(tim^{Me})$_3$] (**2**) presents some unique features, which require some further comments. To the best of our knowledge, all described poly(mercaptoimidazolyl)borates and respective transition metal complexes present ^{1}H NMR spectra with a characteristic pair of doublets for the two CH protons (H(4) and H(5)) of the mercaptoimidazolyl rings, as we have found for ligand **1** and for complexes **3** and **4**.[15,25–43] By contrast, in the ^{1}H NMR spectrum of compound **2** we have found an unique doublet at 6.61 ppm, showing the usual coupling constant of the CH protons of mercaptoimidazole (J = 2.1 Hz) and integrating for three protons, while the remaining mercaptoimidazolyl C–H protons originate a quite broad signal centered at 6.80 ppm. (see Fig. 1). The attribution of this broad resonance to the mercaptoimidazolyl C–H protons was based on a 2D homonuclear [^{1}H, ^{1}H] COSY experiment, which demonstrated that the broad resonance is coupled with the doublet appearing at 6.61 ppm, unambiguously assigned to one of the C–H protons (H(4) and H(5)) of the mercaptoimidazole rings. The broadening is certainly related with the quadrupolar moment of ^{11}B,[44] and the broad resonance must correspond to the H(5) proton which is closer to the boron atom (see Fig. 1 for atom numbering). This has been confirmed by a 1D ^{1}H NOESY NMR experiment. The selective irradiation of the mercaptoimidazole N–CH$_3$ protons, resonating at 3.41 ppm, enhanced the doublet at 6.61 ppm which, therefore, corresponds to the H(4) methyne protons.

For [Re{MeB(tim^{Me})$_3$-κ^3*S*,*S*,*S*}(CO)$_3$] (**3**), the above discussed IR and ^{1}H NMR spectroscopic data are consistent with the solid state molecular structure of the complex, which was obtained by X-ray diffraction analysis. The structure of **3** consists of discrete mononuclear units with the rhenium atom in a slightly distorted octahedral environment. There are two molecules per asymmetric unit which are crystallographically independent but chemically equivalent. The ORTEP view of one of the molecules is shown in Fig. 2. Selected bond distances and angles are given in Table 2.

Table 2 Selected bond lengths (Å) and angles (°) for **3**

Molecule 1			
Re(1)–C(1)	1.894(13)	Re(1)–C(2)	1.910(12)
Re(1)–C(3)	1.88(2)	Re(1)–S(1)	2.526(3)
Re(1)–S(2)	2.527(3)	Re(1)–S(3)	2.509(3)
C(1)–O(1)	1.155(13)	C(2)–O(2)	1.129(12)
C(3)–O(3)	1.154(15)	B(1)–C(10)	1.62(2)
C(1)–Re(1)–C(2)	89.3(5)	C(1)–Re(1)–C(3)	91.9(6)
C(2)–Re(1)–C(3)	90.5(6)	C(1)–Re(1)–S(1)	91.6(4)
C(1)–Re(1)–S(2)	176.5(4)	C(1)–Re(1)–S(3)	86.8(4)
C(2)–Re(1)–S(1)	177.8(4)	C(2)–Re(1)–S(2)	90.2(4)
C(2)–Re(1)–S(3)	90.0(4)	C(3)–Re(1)–S(1)	87.5(5)
C(3)–Re(1)–S(2)	91.5(4)	C(3)–Re(1)–S(3)	178.6(4)
S(1)–Re(1)–S(2)	88.97(10)	S(1)–Re(1)–S(3)	92.01(10)
S(2)–Re(1)–S(3)	89.76(10)		
Molecule 2			
Re(2)–C(4)	1.896(12)	Re(2)–C(5)	1.89(2)
Re(2)–C(6)	1.876(15)	Re(2)–S(4)	2.537(3)
Re(2)–S(5)	2.525(3)	Re(2)–S(6)	2.505(3)
C(4)–O(4)	1.148(12)	C(5)–O(5)	1.161(15)
C(6)–O(6)	1.156(14)	B(2)–C(20)	1.58(2)
C(4)–Re(2)–C(5)	89.9(5)	C(4)–Re(2)–C(6)	90.1(5)
C(5)–Re(2)–C(6)	90.1(6)	C(4)–Re(2)–S(4)	177.7(3)
C(4)–Re(2)–S(5)	92.0(4)	C(4)–Re(2)–S(6)	87.4(4)
C(5)–Re(2)–S(4)	89.4(4)	C(5)–Re(2)–S(5)	177.8(4)
C(5)–Re(2)–S(6)	90.5(4)	C(6)–Re(2)–S(4)	92.0(4)
C(6)–Re(2)–S(5)	88.8(5)	C(6)–Re(2)–S(6)	177.5(4)
S(4)–Re(2)–S(5)	88.73(10)	S(4)–Re(2)–S(6)	90.41(9)
S(5)–Re(2)–S(6)	90.78(11)		

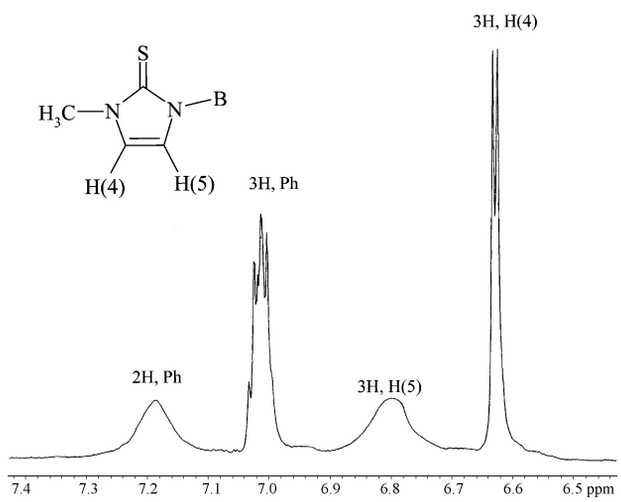


Fig. 1 ^{1}H NMR spectrum of Li[RB(tim^{Me})$_3$] (**2**) in the aromatic region, displaying an insert with the numbering of mercaptoimidazole hydrogens.

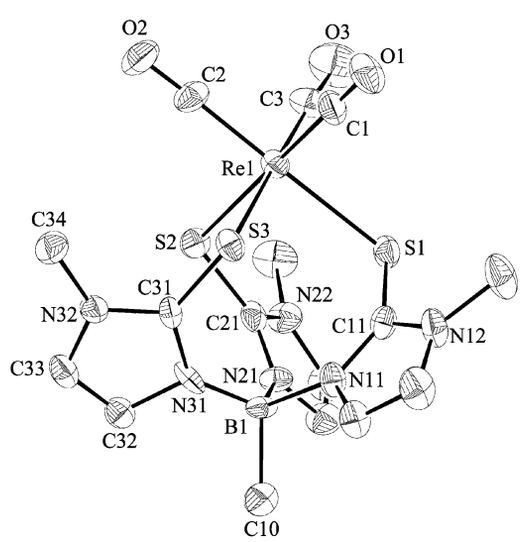


Fig. 2 ORTEP view of **3**. Vibrational ellipsoids are drawn at the 30% probability level.

The carbonyl ligands occupy one face of the coordination polyhedra, with an average Re–C distance of 1.892(12) Å. The three remaining coordination positions are occupied by the thione sulfur atoms, with an average Re–S bond distance of 2.521(12) Å. These metrical parameters are comparable to those that we have previously reported for the congener [Re{$HB(tim^{Me})_3$-κ^3*S*,*S*,*S*}$(CO)_3$] (av. Re–C, 1.904(9) Å; av. Re–S, 2.516(2) Å).[15] With the exception of the presence of the methyl group in **3**, the molecular structure of both complexes are almost superimposable and, therefore, the structure of **3** does not justify a more exhaustive discussion.

Conclusions

The first examples of tris(mercaptoimidazolyl)borates bearing alkyl or aryl substituents directly attached to the boron atom have been prepared. These novel ligands, $Li[RB(tim^{Me})_3]$ (R = Me (**1**), Ph (**2**)) were used to prepare the Re(I) tris(carbonyl) complexes [Re{$RB(tim^{Me})_3$-κ^3*S*,*S*,*S*}$(CO)_3$] (R = Me (**3**), Ph (**4**)), which are quite resistant toward hydrolysis and aerial oxidation. Compounds **3** and **4** can be seen as valuable models for the development of specific radiopharmaceuticals. Our research group is currently evaluating the possibility of replacing the methyl or phenyl groups in ligands **1** and **2** by biologically relevant substrates, aiming to explore further these systems in biomedical applications.

Acknowledgments

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References

1 A. Alberto, R. Schibli, A. Egli, A. P. Schubiger, U. Abram and T. A. Kaden, *J. Am. Chem. Soc.*, 1998, **120**, 7987.
2 A. Hoepping, M. Reisgys, P. Brust, S. Seifert, H. Spies, R. Alberto and B. Johannsen, *J. Med. Chem.*, 1998, **41**, 4429.
3 A. Alberto, R. Schibli, R. Waibel, U. Abram and A. P. Schubiger, *Coord. Chem. Rev.*, 1999, **190–192**, 901.
4 A. Alberto, R. Schibli, A. Egli, A. P. Schubiger, U. Abram, H.-J. Pietzsch and B. Johannsen, *J. Am. Chem. Soc.*, 1999, **121**, 6076.
5 A. Egli, A. Alberto, L. Tannahill, R. Schibli, U. Abram, A. Schaffland, R. Waibel, D. Tourwé, L. Jeannin, K. Iterbeke and A. P. Schubiger, *J. Nucl. Med.*, 1999, **40**, 1913.
6 R. Waibel, R. Alberto, J. Willuda, R. Finnern, R. Schibli, A. Stichelberger, A. Egli, U. Abram, J.-P. Mach, A. Plueckthun and P. A. Schubiger, *Nat. Biotechnol.*, 1999, **17**, 897.
7 R. Schibili, R. La Bella, R. Alberto, E. Garcia-Garayoa, K. Ortner, U. Abram and A. P. Schubiger, *Bioconjugate Chem.*, 2000, **11**, 345.
8 H.-J. Pietzsch, R. Schibli, R. La Bella, R. Alberto, E. G. Garayoa, K. Ortner, A. AbramGupta, M. Reisgys, A. Drews, S. Seifert, R. Syhre, H. Spies, R. Alberto, U. Abram, P. A. Schubiger and B. Johannsen, *Bioconjugate Chem.*, 2000, **11**, 414.
9 J. Wald, R. Alberto, K. Ortner and L. Candreia, *Angew. Chem., Int. Ed.*, 2001, **40**, 3062.
10 J. Petrig, R. Schibili, C. Dumas, R. Alberto and P. A. Schubiger, *Chem. Eur. J.*, 2001, **7**, 1868.
11 J. D. G. Correia, A. Domingos, I. Santos, R. Alberto and K. Ortner, *Inorg. Chem.*, 2001, **40**, 5147.
12 J. F. Valliant, P. Morel, P. Schaffer and J. H. Kaldis, *Inorg. Chem.*, 2002, **41**, 628.
13 S. R. Banerjee, M. K. Levadala, N. Lazarova, L. Wei, J. F. Valliant, K. A. Stephenson, J. W. Babich, K. P. Maresca and J. Zubieta, *Inorg. Chem.*, 2002, **41**, 6417.
14 J. Bernard, K. Ortner, B. Spingler, H.-J. Pietzsch and R. Alberto, *Inorg. Chem.*, 2003, **42**, 1014.
15 (*a*) R. Garcia, A. Paulo, A. Domingo, I. Santos, K. Ortner and R. Alberto, *J. Am. Chem. Soc.*, 2000, **122**, 11240; (*b*) R. Garcia, A. Paulo, A. Domingos and I. Santos, *J. Organomet. Chem.*, 2001, **632**, 41; (*c*) R. Garcia, A. Domingos, A. Paulo, I. Santos and R. Alberto, *Inorg. Chem.*, 2002, **41**, 2422; (*d*) R. Garcia, Y. H. Xing, A. Paulo, A. Domingos and I. Santos, *J. Chem. Soc., Dalton Trans.*, 2002, 4236.
16 R. Garcia, A. Paulo, L. Gano and I. Santos, unpublished results.
17 J. R. Dilworth and S. J. Parrott, *Chem. Soc. Rev.*, 1998, **27**, 43.
18 A. Alberto, A. Egli, U. Abram, K. Hegetschweiler, V. Gramlich and P. A. Schubiger, *J. Chem. Soc., Dalton Trans.*, 1994, 2815.
19 B. Singaram, T. E. Cole and C. H. Brown, *Organometallics*, 1984, **3**, 774.
20 C. K. Fair, MOLEN; Enraf-Nonius, Delft, The Netherlands, 1990.
21 G. M. Sheldrick, SHELXS-86: Program for the Solution of Crystal Structure, University of Göttingen, Germany, 1986.
22 G. M. Sheldrick, SHELXL-93: Program for the Refinement of Crystal Structure, University of Göttingen, Germany, 1993.
23 L. Farrugia, *J. Appl. Crystallogr.*, 1997, **32**, 565.
24 J. L. Kisko, T. Hascall, C. Kimblin and G. Parkin, *J. Chem. Soc., Dalton Trans.*, 1999, 1929 and references therein.
25 J. F. Ojo, P. A. Slavin, J. Reglinsli, M. Garner, M. D. Spicer, A. R. Kennedy and S. J. Teat, *Inorg. Chim. Acta*, 2001, **313**, 15.
26 M. Garner, J. Reglinski, I. Cassidy, M. D. Spicer and A. R. Kennedy, *Chem. Commun.*, 1996, 19.
27 C. Kimblin, T. Hascall and G. Parkin, *Inorg. Chem.*, 1997, **36**, 5680.
28 C. Santini, G. G. Lobbia, C. Pettinari, M. Pellei, G. Valle and S. Calogero, *Inorg. Chem.*, 1998, **37**, 890.
29 C. Santini, C. Pettinari, G. G. Lobbia, R. Spagna, M. Pellei and F. Vallorani, *Inorg. Chim. Acta*, 1999, **285**, 81.
30 J. Reglinski, M. Garner, I. D. Cassidy, P. A. Slavin, M. D. Spicer and D. R. Armstrong, *J. Chem. Soc., Dalton Trans.*, 1999, 2119.
31 J. Reglinski, M. D. Spicer, M. Garner and A. R. Kennedy, *J. Am. Chem. Soc.*, 1999, **121**, 2317.
32 C. Kimblin, B. M. Bridgewater, D. G. Churchill and G. Parkin, *Chem. Commun.*, 1999, 2301.
33 A. F. Hill, G. R. Owen, A. J. P. White and D. J. Williams, *Angew. Chem., Int. Ed.*, 1999, **38**, 2759.
34 C. Kimblin, B. M. Bridgewater, D. G. Churchill, T. Hascall and G. Parkin, *Inorg. Chem.*, 2000, **39**, 4240.
35 C. Kimblin, B. M. Bridgewater, T. Hascall and G. Parkin, *J. Chem. Soc., Dalton Trans.*, 2000, 891.
36 C. Kimblin, B. M. Bridgewater, T. Hascall and G. Parkin, *J. Chem. Soc., Dalton Trans.*, 2000, 1267.
37 P. A. Slavin, J. Reglinski, M. D. Spicer and A. R. Kennedy, *J. Chem. Soc., Dalton Trans.*, 2000, 239.
38 B. M. Bridgewater, T. Filleben, R. A. Friesner and G. Parkin, *J. Chem. Soc., Dalton Trans.*, 2000, 4494.
39 M. Tesmer, M. Shu and H. Vahrenkamp, *Inorg. Chem.*, 2001, **40**, 4022.
40 C. Kimblin, D. G. Churchill, B. M. Bridgewater, J. N. Girard, D. A. Quarless and G. Parkin, *Polyhedron*, 2001, **20**, 1891.
41 G. G. Lobbia, C. Pettinari, C. Santini, N. Somers, B. W. Skelton and A. H. White, *Inorg. Chim. Acta*, 2001, **319**, 15.
42 M. Garner, M.-A. Lehmann, J. Reglinski and M. D. Spicer, *Organometallics*, 2001, **20**, 5233–5236.
43 S. Bakbak, C. D. Incarvito, A. L. Rheingold and D. Rabinovich, *Inorg. Chem.*, 2002, **41**, 998.
44 H. Nöth and B. Wrackmeyer, in *Nuclear Magnetic Resonance Spectroscopy of Boron Compounds*, Springer-Verlag, Berlin, 1978.