Inorganic Chemistry Communications 14 (2011) 238–242

Contents lists available at ScienceDirect

Inorganic Chemistry Communications

journal homepage: www.elsevier.com/locate/inoche

Rhenium(I) and technetium(I) complexes of a novel pyridyltriazole-based ligand containing an arylpiperazine pharmacophore: Synthesis, crystal structures, computational studies and radiochemistry

Achour Seridi [a,b,1], Mariusz Wolff [c,1], Alexandre Boulay [a,b], Nathalie Saffon [d], Yvon Coulais [e], Claude Picard [a,b], Barbara Machura [c,*], Eric Benoist [a,b,*]

[a] *CNRS, Laboratoire de Synthèse et Physico-Chimie de Molécules d'Intérêt Biologique, SPCMIB, UMR 5068, 118, Route de Narbonne, F-31062 Toulouse Cedex 9, France*
[b] *Université de Toulouse, UPS, Laboratoire de Synthèse et Physico-Chimie de Molécules d'Intérêt Biologique, SPCMIB, UMR 5068, 118, Route de Narbonne, F-31062 Toulouse Cedex 9, France*
[c] *Department of Crystallography, Institute of Chemistry, University of Silesia, 9th Szkolna St., 40-006 Katowice, Poland*
[d] *Université de Toulouse, UPS and CNRS, Structure Fédérative Toulousaine en Chimie Moléculaire SFTCM FR2599, 118, Route de Narbonne, F-31062 Toulouse Cedex 9, France*
[e] *Laboratoire "Traceurs et traitement de l'image", Faculté de Médecine de Purpan, EA 3033, 133, Route de Narbonne, 31062 Toulouse Cedex 9, France*

ARTICLE INFO

Article history:
Received 16 September 2010
Accepted 3 November 2010
Available online 10 November 2010

Keywords:
Click chemistry
Bidentate ligands
Rhenium
Technetium
X-ray structure
DFT calculations

ABSTRACT

The preparation of two $M(CO)_3$ complexes ($M = Re$ and ^{99m}Tc) from a novel pyridyltriazole-based ligand **2** bearing the bioactive (2-methoxyphenyl)piperazine pharmacophore are described. Spectral data, X-ray structure and DFT calculations of the rhenium(I) complex as well as the ^{99m}Tc-labelling of **2** are reported. Both complexes were neutral and iso-structural. Moreover, the ^{99m}Tc-complex presented a suitable lipophilic character for its use as a CNS imaging agent.

Over the past decade, the coordination chemistry of tricarbonyl technetium(I) and tricarbonyl rhenium(I) cores has been intensively studied, mainly due to the easy production of the hydrophilic air-stable *fac*-$[M(CO)_3(H_2O)_3]^+$ precursor from the corresponding permetallates MO_4^- ($M = {}^{99m}Tc$ or $^{186/188}Re$), and the extensive use of the ^{99m}Tc and $^{186/188}Re$ radioisotopes in the development of diagnostic and therapeutic radiopharmaceuticals, respectively [1]. Interestingly, the $^{185/187}Re(CO)_3$ complexes, which have been commonly used as a non-radioactive alternative to technetium complexes for macroscopic-scale synthesis and structural characterization, also could serve as luminescent probes. In this latter case, the tricarbonyl rhenium core was coordinated by heteroaromatic amine, e.g., diquinolinylamine (dqa) [2], or α,α′-diimine such as 2,2′-bipyridine [3]. It is noteworthy that if Zubieta et al. developed maleimide-dqa derivatives, leading to $M(CO)_3^+$ complexes suitable for both imaging and radioimaging studies of proteins [4], the development of functionalized bipyridines still remains a significant challenge.

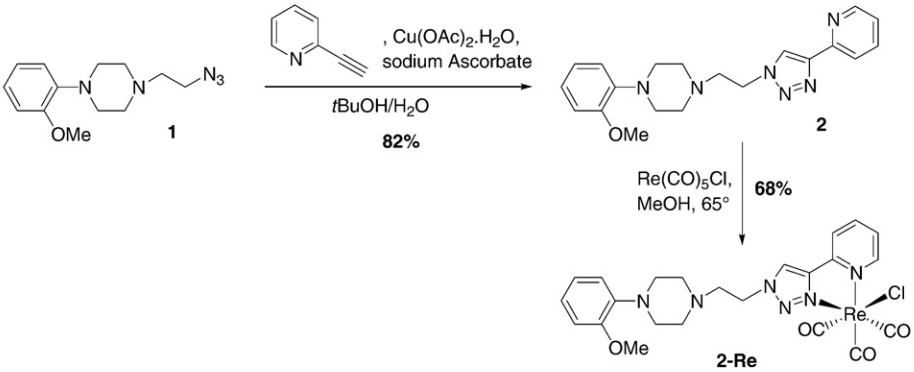
Within this context and aiming at the development of novel rhenium (I) and technetium(I) complexes as luminescent and/or radiopharmaceutical agents, we recently designed fluorescent rhenium(I) complexes from mono-functionalized 2-pyridyl-1,2,3-triazole derivatives (or pyta) as alternative ligands to 2,2′-bipyridines [5]. The mild reaction conditions associated with the synthetic click approach allowed the preparation of a large number of mono-functionalized pyta derivatives. Nevertheless, only a few of them possess a tethering group for further coupling to a biomolecule [5,6], and one example of pyta grafted on a bioactive molecule (a glucose scaffold) was reported [7].

As a continuation of our research, in the present study, we described a convenient synthesis of a novel pyta functionalized by the bioactive (2-methoxyphenyl)piperazine moiety, this pharmacophore being found in numerous selective $5\text{-}HT_{1A}$ imaging agents [8]. The preparation of this ligand as well as the investigation of its coordinating ability with a tricarbonyl rhenium core has been herein presented. Definitive characterization of the tricarbonyl rhenium(I) complex **2-Re**, of general formula $[Re(CO)_3Cl(\kappa^2\text{-}\mathbf{2})]$, was accomplished by X-ray crystallography study and DFT calculations. Since bidentate diimine are excellent ligands for the $^{99m}Tc(CO)_3^+$ core, we also investigated the labelling of the pyta derivative with ^{99m}Tc.

---

[*] Corresponding authors. E. Benoist is to be contacted at the Université de Toulouse; UPS; Laboratoire de Synthèse et Physico-Chimie de Molécules d'Intérêt Biologique, SPCMIB, UMR 5068, 118, Route de Narbonne, F-31062 Toulouse Cedex 9, France. Tel.: +33 5 61 55 64 80; fax: +33 5 61 55 60 11.
E-mail addresses: basia@ich.us.edu.pl (B. Machura), benoist@chimie.ups-tlse.fr (E. Benoist).
[1] Both authors equally contributed to the experiments.

1387-7003/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.inoche.2010.11.002



Scheme 1.

In order to minimize sterical interference between the metallic chelating centre and the receptor binding part, an ethylene bridge was used as a spacer. Thus, the azido-ligand **1**, prepared by a three step procedure, starting from the commercial chlorhydrate of (2-methoxyphenyl)piperazine, was obtained in a 51% overall yield [9]. Compound **1** undergoes the click reaction with 2-ethynylpyridine to afford a pyta derivative containing the (2-methoxyphenyl)piperazine pharmacophore (scheme 1). In this case, the copper(II) salt/reducing agent system (Cu (OAc)$_2$.H$_2$O, 20 mol.%/sodium ascorbate, 40 mol.%) revealed to be a better efficient catalyst than copper(I) species used directly [10]. Compound **2** was fully characterized by classical spectroscopic methods [11]. Crystals of **2** suitable for X-ray diffraction were obtained by the slow evaporation of a dichloromethane/methanol solution [12]. Structural features compare well to those observed for related pyta derivatives [13]. Compound **2** exhibits an *anti* arrangement adopted by the N(5) and N(6) atoms of the triazole and pyridine rings, respectively, and an azo character of the 1,2,3-triazole ring, the N = N bond distance of the 1,2,3-triazole ring being shorter than the adjacent N–C and N–N bonds (N(4) = N(5) = 1.3133(15) Å *vs.* N(5)–C(15) = 1.3633(15) Å and N(4)–N(3) = 1.3492(14) Å). Interestingly, a significant contribution to crystal cohesion is provided by a network of intra-layer hydrogen bonds in which the ligand and one lattice water molecule participate. The lattice water molecule forms O–H···N bonds with one nitrogen of the piperazinyl moiety of **2** (d(O(2)–H(2a)…N(2)) = 3.013 Å, O(2)–H(2a)–N(2) = 173.08°).

The rhenium complex **2-Re** was prepared in moderate yield by reacting ligand **2** with a slight excess of the Re(CO)$_5$Cl precursor in refluxing methanol (1.2:1 metal:ligand ratio). It was characterized by the usual analytical techniques [11], including X-ray diffraction analysis. The positive-ion DCI-MS spectrum of **2-Re** showed the parent peak $[M+H]^+$ with the correct isotope distribution pattern without significant fragmentation. The facial arrangement of the carbonyl groups is evidenced from the CO-stretching absorptions in the IR spectrum. The three strong ν(CO) stretching bands appear in the region of 2021–1896 cm^{-1}, indicating the presence of the *fac*-[Re (CO)$_3$]$^+$ core [14]. In ^{1}H NMR, a significant down-field shift (0.3 ppm) of the signal for the triazole proton was observed, as expected [11]. Interestingly, the hydrogen resonances of the (2-methoxyphenyl) piperazine moiety were either unchanged or exhibited very minor shifts compared to those of the free ligand. The lack of appreciable shifts confirms the pendant nature of the (2-methoxyphenyl) piperazine framework. Therefore, interaction of the metal centre with the bioactive part of the molecule can largely be excluded. This structural feature was confirmed by the X-ray diffraction analysis of **2-Re** [15]. As anticipated, the ethylene bridge keeps the (2-methoxyphenyl)piperazine group at a large distance from the chelating part of the molecule (Fig. 1), and precludes neither any coordinative or hydrogen-bonding interactions with components near the coordination sphere, nor the folding of the pendant arm towards the metal center, this latter feature being observed with more flexible spacers, as reported by Santos group [16]. The fact that the bioactive fragment does not interact significantly with the metal should suggest a suitable affinity for the 5-HT$_{1A}$ receptors.

The coordination geometry about rhenium in **2-Re** is distorted octahedral, as illustrated by the ORTEP view (Fig. 1). The three CO ligands are coordinated to one face of the octahedron, maximizing Re–CO back-bonding, whereas the other face is occupied by the chlorine and the bidentate pyta ligand, leading to a neutral complex. Corresponding bond lengths and angles in **2-Re** are unexceptional (Fig. 1) and compare well to those observed for related complexes [5,7]. The Re–carbonyl bond lengths average 1.93 Å and lie in the middle side of the range (1.92–1.94 Å) found for other tricarbonyl–rhenium pyta derivatives [7]. Conversely, the Re(1)–Cl(1) distance (2.4657 Å) is the shortest observed in the Re(CO)$_3$ complexes based on pyta moieties (mean 2.471–2.485 Å) [5,7]. The *trans* bond angles fall in the range of 172.1–176.6°, showing only moderate deviations from an idealized octahedral geometry. The most significant angular distortion is associated with the bite angle N–Re–N angle of 74.83°. This value is a consequence of the formation of a strained five-membered chelate ring.

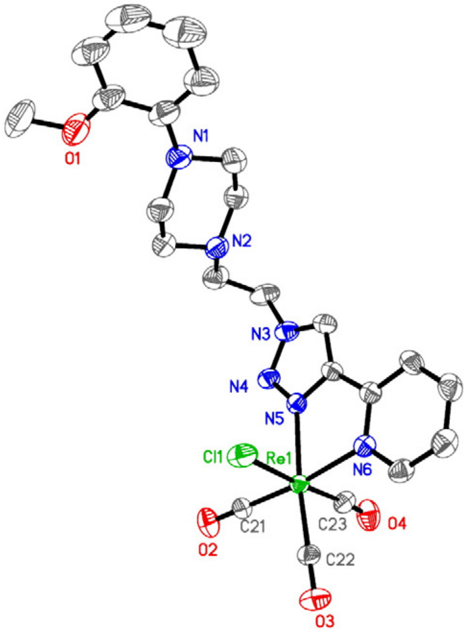


Fig. 1. Molecular structure of **2-Re** (ellipsoids drawn at 50% probability level); hydrogen atoms have been omitted for clarity. Selected bond parameters: Re(1)–Cl(1) = 2.4657 (10), Re(1)–N(5) = 2.161(3), Re(1)–N(6) = 2.210(3), Re(1)–C(21) = 1.921(4), Re(1)–C(22) = 1.909(4), Re(1)–C(23) = 1.957(4), N(3)–N(4) = 1.346(4) Å; C(23)–Re(1)–Cl (1) = 176.63(11), C(22)–Re(1)–N(5) = 172.11(13), C(21)–Re(1)–N(6) = 173.82(14), C(23)–Re(1)–N(5) = 93.70(13), C(23)–Re(1)–N(6) = 92.56(13), and N(5)–Re(1)–N (6) = 74.83(11)°.

The gas phase geometry of **2-Re** was optimized in a closed-shell singlet ($S=1$) state without any symmetry restrictions with the DFT method using the hybrid B3LYP functional of GAUSSIAN-03 [17,18]. The calculations were performed using the ECP LANL2DZ basis set [19] with an additional *d* and *f* functions with the exponents $\alpha=0.3811$ and $\alpha=2.033$ [20] for the rhenium and the standard 6-31G basis set for the other atoms, respectively. For chlorine, nitrogen and oxygen diffuse and polarization functions were added [21,22]. The vibrations in the calculated vibrational spectrum of **2-Re** were real; thus, the geometry of **2-Re** corresponds to true energy minimum. The predicted bond lengths and angles are in reasonable agreement with the values based on the X-ray crystal structure data, and the general trends observed in the experimental data are well reproduced in the calculations [23].

The partial molecular orbital diagram of **2-Re** with several occupied and virtual molecular orbital contours is presented in Fig. 2. The HOMO–LUMO gap is equal to 3.32 eV. The low-lying virtual orbitals correspond mainly to the π-antibonding orbitals of the chelate and carbonyl ligands. The LUMO and LUMO + 1 are centered at the 2-pyridyl-1,2,3-triazole fragment of the chelate ligand. The higher virtual orbitals are delocalized among the carbonyls and Re atom or among carbonyls, Re and chelate ligand. The three highest occupied molecular orbitals are localized on the (2-methoxyphenyl)piperazine part of the chelate ligand. The HOMO-3, HOMO-4 and HOMO-5 are predominantly of d_{Re} orbital character corresponding to the $(5d^{2}_{xy})$ $(5d_{\pi})^4$ occupation.

The electronic spectrum of **2-Re** was calculated with the TDDFT method [24], and the solvent effect (methanol) was simulated using the polarizable continuum model with the integral equation formalism (IEF–PCM) [25]. The experimental and calculated electronic spectra of **2-Re** are compared in Fig. 3. Each calculated transition is represented by

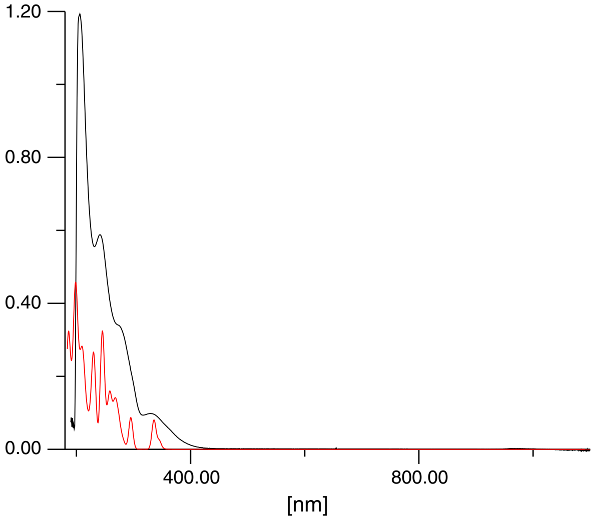


Fig. 3. Experimental (black) and calculated (red) electronic absorption spectra of **2-Re**; λ_{max} [nm] (ε [$dm^3\ mol^{-1}\ cm^{-1}$]): 329.9 (3270), 276.8 (11250), 241.1 (19650), and 206.1 (39730).

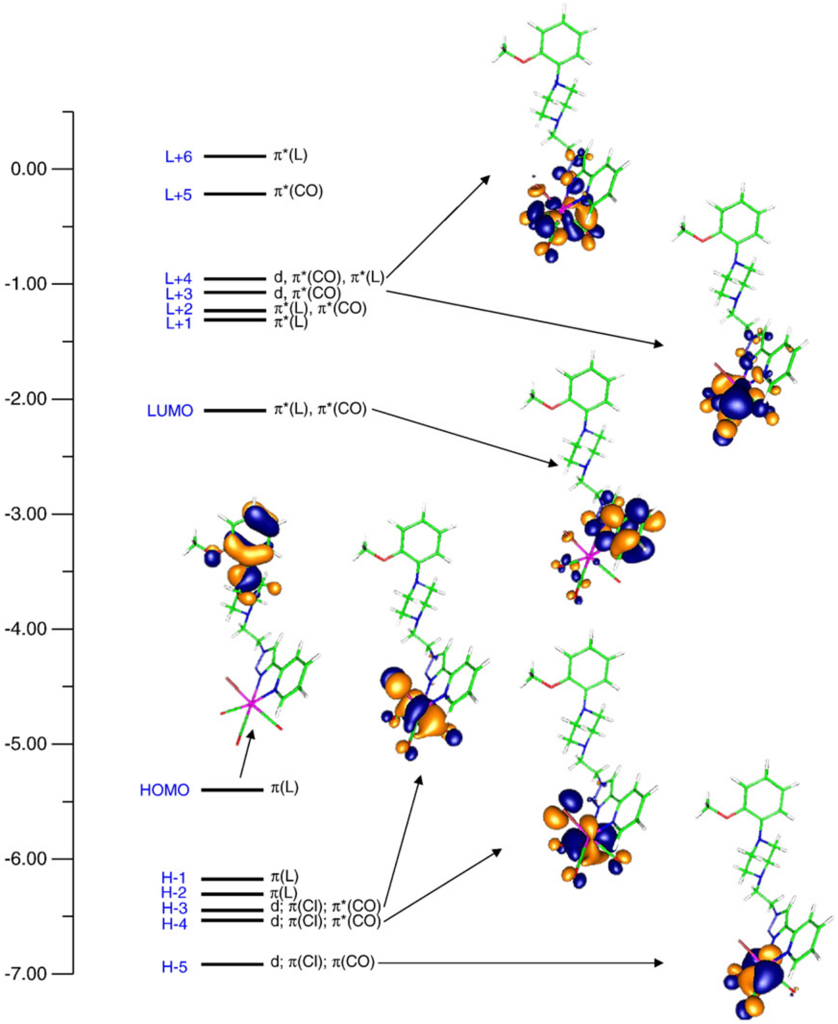


Fig. 2. Energy (eV), character and some contours of the occupied and unoccupied molecular orbitals of **2-Re**.

a Gaussian function $y = ce^{-bx^2}$ with the height (*c*) equal to the oscillator strength and *b* equal to 0.04 nm^{-2}. The TDDFT/PCM calculations well reproduce the absorption spectrum of **2-Re** in methanol. The assignment of the calculated orbital excitations to the experimental bands was based on an overview of the contour plots and relative energy to the occupied and unoccupied orbitals involved in the electronic transitions. The longest wavelength experimental band of the rhenium complex at 329.9 nm originates in the HOMO-1 → LUMO, HOMO-1 → LUMO + 1 and HOMO-4 → LUMO transitions. As shown in Fig. 2, the LUMO and LUMO + 1 orbitals are centered at the 2-pyridyl-1,2,3-triazole part of the chelate ligand, the HOMO-1 orbital has a substantial contribution from the free electron pairs on the nitrogen atoms of the piperazine ring, whereas the HOMO-4 is delocalized on the whole $Re(CO)_3Cl$ unit. Accordingly, the transitions assigned to the longest wavelength experimental bands can be seen as mixed $d_{Re} \rightarrow \pi^*$(chelate) (MLCT) and π(Cl)/π(chelate) $\rightarrow \pi^*$(chelate) (LLCT) or a delocalized MLLCT (*metal–ligand–ligand CT*) description can be used.

The experimental absorption bands at 276.8, 241.1 and 206.1 nm are attributed to the *metal-to-ligand charge transfer* (occurring from the rhenium ion to the π-antibonding orbitals of the chelate ligand or π-antibonding orbitals of the carbonyl groups), *ligand–ligand charge transfer* and intraligand (IL) transitions (see Table 1 in supplementary data). As expected, **2-Re** exhibited fluorescence at room temperature in the MeOH solution ($\lambda_{exc} = 330$ nm, and $\lambda_{em} = 522$ nm) [26]. Its observed that the quantum yield (Φ = 0.32%) is in agreement with the values measured for other Re(I) complexes of the type [Re(α,α′ diimine)$(CO)_3$X] (α,α′-diimine = 2,2′-bipy or pyta, X = halogene) [7].

The technetium-99m being one of the most relevant isotopes for imaging purposes, the ^{99m}Tc-labelling of **2** was evaluated. The radiocomplex **2-^{99m}Tc** was prepared in excellent yield (>95%) using the *fac*-$[^{99m}Tc(CO)_3(H_2O)_3]^+$ precursor (see supplementary data). After 20°min at 80°C, $[^{99m}Tc(CO)_3(H_2O)_3]^+$ had disappeared completely and the formation of a new product, **2-^{99m}Tc**, was observed in the radiochromatogram. Its radiochemical purity assessed by ITLC was >98% after RP-HPLC purification. In addition, we demonstrated that the radiolabelling of **2** could be performed at room temperature but it required a longer reaction time. The chemical identity of **2-^{99m}Tc** was determined by comparing its analytical HPLC profile with the HPLC profile of the rhenium analog **2**. Since the retention time of the ^{99m}Tc-complex is similar to that of the "cold" Re-complex (11.9°min for **2-Re** *vs.* 11.3°min for **2-^{99m}Tc**), it may be assumed that identical structures are adopted by the species generated at the tracer level and the complex produced and characterized on the macroscopic scale. As previously reported by several teams, the chlorine atom present in the radiolabelling medium replaces one of the H_2O ligands of the $[^{99m}Tc(CO)_3(H_2O)_3]^+$ precursor (thermodynamically favoured process) [16,27], leading after reaction with **2**, to the formation of the neutral complex **2-^{99m}Tc** of general formula [$^{99m}Tc(CO)_3Cl($ ^{2}-**2**)].

The lipophilic character of this radiocomplex was assessed by the determination of the partition coefficient (P) in physiological conditions (0.1°M phosphate buffer pH 7.4/n-octanol) and was expressed as $\log P_{o/w}$. A value of 2.34 was found, indicating that **2-^{99m}Tc** is moderately lipophilic. It is noteworthy that this value is within the range for related radiocomplexes able to cross the blood brain barrier ($\log P_{o/w} = 0.5–2.5$) [28].

In short, a novel pyta derivative grafted to a bioactive pharmacophore was prepared, taking advantage of the trendy click chemistry. The corresponding rhenium and technetium complexes were characterized in the solid and solution states. If a Tc- or Re-tricarbonyl complex with a tridentate ligand is less prone to cross-metallation, previous studies showed that this kind of bidentate $M(CO)_3^+$ complexes with a chlorine ligand (at the sixth position) was suitable for *in vivo* work and exhibited high stability against histidine and cysteine challenge experiments [27a]. Thus, this bidentate ligand **2** can be considered: (i) a good starting point for the preparation of novel technetium-99m $5HT_{1A}$ imaging probes and (ii) an alternative of $5HT_{1A}$ imaging probes based on PET emitters. Then, the neutrality and the lipophilic character of both metallic complexes are two important prerequisites for the design of central nervous system (CNS) receptor-binding agents. The binding affinity and *in vivo* biodistributions of **2-^{99m}Tc** will be reported in another paper.

Acknowledgements

The Gaussian-03 calculations were carried out in the Wrocław Centre for Networking and Supercomputing, WCSS, Wrocław, Poland, http://www.wcss.wroc.pl.

Appendix A. Supplementary material

See the supplementary data for the materials and equipment, the synthesis of compounds **2** and **2-Re** and Table 1. CCDC 787115 and CCDC 787116 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via http://www.ccdc.cam.ac.uk/data_request/cif. Supplementary materials related to this article can be found online at doi:10.1016/j.inoche.2010.11.002.

References

[1] (a) R. Schibli, R. Schwarzbach, R. Alberto, K. Otner, H. Schmalle, C. Dumas, A. Egli, P.A. Schubiger, Bioconjug. Chem. 13 (2002) 750;
(b) R. Alberto, K. Otner, N. Weathley, R. Schibli, P.A. Schubiger, J. Am. Chem. Soc. 123 (2001) 3135.

[2] (a) K.A. Stephenson, S.R. Banerjee, T. Besanger, O.O. Sogbein, M.K. Levadala, N. McFarlane, J.A. Lemon, D.R. Boreham, K.P. Maresca, J.D. Brennan, J.W. Babich, J. Zubieta, J.F. Valliant, J. Am. Chem. Soc. 126 (2004) 8598;
(b) P. Schaffer, J.A. Gleave, J.A. Lemon, L.C. Reid, L.K.K. Pacey, T.H. Farncombe, D.R. Boreham, J. Zubieta, J.W. Babich, L.C. Doering, J.F. Valliant, Nucl. Med. Biol. 35 (2008) 159.

[3] A. Coleman, C. Brennan, J.G. Vos, M.T. Pryce, Coord. Chem. Rev. 252 (2008) 2585.

[4] (a) S.R. Banerjee, J.W. Babich, J. Zubieta, Chem. Commun. (2005) 1784;
(b) S.R. Banerjee, P. Schaffer, J.W. Babich, J.F. Valliant, J. Zubieta, Dalton Trans. (2005) 3886.

[5] (a) A. Boulay, Master's thesis, Paul Sabatier University, Toulouse, France, 2009b A. Boulay, C. Picard, E. Benoist, in: U. Mazzi, W.C. Eckelman, W.A. Volkert (Eds.), Technetium and other radiometals in chemistry and medicine, SGE Editoriali, Padova, Italy, 2010, pp. 111–112.

[6] B. Happ, C. Friebe, A. Winter, M.D. Hager, R. Hoogenboom, U.S. Schubert, Chem. Asian J. 4 (2009) 154.

[7] M. Obata, A. Kitamura, A. Mori, C. Kameyama, J.A. Czaplewska, R. Tanaka, I. Kinoshita, T. Kusumoto, H. Hashimoto, M. Harada, Y. Mikata, T. Funabiki, S. Yano, Dalton Trans. (2008) 3292.

[8] (a) J. Passchier, A. van Waerde, Eur. J. Nucl. Med. 28 (2001) 113;
(b) I. Heimbold, A. Drews, R. Syhre, M. Kretzschmar, H.-J. Pietzsch, B. Johannsen, Eur. J. Nucl. Med. 29 (2002) 82;
(c) M. Saidi, S. Seifert, M. Kretzschmar, R. Bergmann, H.-J. Pietzsch, J. Organomet. Chem. 689 (2004) 4739;
(d) R. Garcia, L. Gano, L. Maria, A. Paulo, I. Santos, H. Spies, J. Biol. Inorg. Chem. 11 (2006) 769;
(e) J.S.D. Kumar, J. Prabhakaran, V.J. Majo, M.S. Milak, S.-C. Hsiung, H. Tamir, N.R. Simpson, R.L. Van Heertum, J.J. Mann, R.V. Parsey, Eur. J. Nucl. Med. Mol. Imaging 34 (2007) 1050;
(f) N. Aznavour, C. Benkelfat, P. Gravel, A. Aliaga, P. Rosa-Neto, B. Bedell, L. Zimmer, L. Descarries, Eur. J. Nucl. Med. Mol. Imaging 36 (2009) 53;
(g) C. Bolzati, N. Salvarese, D. Carta, F. Refosco, A. Dolmella, H.-J. Pietzsch, R. Bergmann, G. Bandoli, J. Biol. Inorg. Chem. (2010), doi:10.1007/s00775-010-0712-4, and references therein.

[9] G. Campiani, S. Butini, F. Trotta, C. Fattorusso, B. Catalanotti, F. Aiello, S. Gemma, V. Nacci, E. Novellino, J.A. Stark, A. Cagnotto, E. Fumagalli, F. Carnovali, L. Cervo, T. Mennini, J. Med. Chem. 46 (2003) 3822.

[10] C. Camp, S. Dorbes, C. Picard, E. Benoist, Tetrahedron Lett. 49 (2008) 1979.

[11] See supplementary data for the synthesis and the characterization of compounds 2 and 2-Re.

[12] Crystal data for 2.H2O: C20H26N6O2, monoclinic, space group P21/c, a = 13.1340 (3), b = 14.5355(3), c = 10.1669(2) Å, α = γ = 90° β = 96.9350(10)° V = 1926.75 (7) Å3, Z = 4, Dc = 1.318 Mg.m-3, 24351 reflections collected, 4753 unique, Rint = 0.0401, data/restraints/parameters: 4753/0/260; S = 1.046; Final R indices [I>2σ(I)] R1 = 0.0401, wR2 = 0.0935; R indices (all data) R1 = 0.0554, wR2 = 0.1020, Largest diff. peak and hole 0.251 and −0.174 e.Å-3, CCDC 787115.

[13] (a) J.D. Crowley, P.H. Bandeen, Dalton Trans. (2010) 612;
(b) D. Schweinfurth, R. Pattacini, S. Strobel, B. Sarkar, Dalton Trans. (2009) 9291.

[14] O. Karagiorgou, G. Patsis, M. Pelecanou, C.P. Raptopoulou, A. Terzis, T. Siatra-Papastaikoudi, R. Alberto, I. Permettis, M. Papadopoulos, Inorg. Chem. 44 (2005) 4118.

[15] Crystal data for 2-Re: C23H24ClN6O4Re, M = 670.13, monoclinic, space group P21/c, a = 20.2441(5), b = 8.6532(2), c = 15.6830(4) Å, $\alpha = \gamma = 90°$ $\beta = 109.1070(10)°$ V = 2595.94(11) Å3, Z = 4, Dc = 1.715 Mg m-3, T = 193(2) K. 33515 reflections collected, 6406 unique, Rint = 0.0478, data/restraints/parameters: 6406/0/317; S = 1.037; Final R indices [$I > 2\sigma(I)$] R1 = 0.0290, wR2 = 0.0749; R indices (all data) R1 = 0.0364, wR2 = 0.0802, Largest diff. peak and hole 1.723 and -1.120 e.Å-3, CCDC 787116.

[16] E. Palma, J.D.G. Correia, A. Domingos, I. Santos, R. Alberto, H. Spies, J. Organomet. Chem. 689 (2004) 4811.

[17] Gaussian 03, Revision D.01, M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery, Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A. D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, and J.A. Pople, Gaussian, Inc., Wallingford CT, 2004.

[18] (a) A.D. Becke, J. Chem. Phys. 98 (1993) 5648;
(b) C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785.

[19] P.J. Hay, W.R. Wadt, J. Chem. Phys. 82 (1985) 299.

[20] K. Eichkorn, F. Weigend, O. Treutler, R. Ahlrichs, Theor. Chem. Acc. 97 (1997) 119.

[21] P.C. Hariharan, J.A. Pople, Theor. Chim. Acta 28 (1973) 213.

[22] V.A. Rassolov, M.A. Ratner, J.A. Pople, P.C. Redfern, L.A. Curtiss, J. Comp. Chem. 22 (2001) 976.

[23] Calculated (experimental) bond lengths [Å]: Re(1)-C(22) = 1.925 (1.909(4)), Re(1)-C(21) = 1.929 (1.921(4)), Re(1)-C(23) = 1.914 (1.957(4)), Re(1)-N(5) = 2.180 (2.161(3)), Re(1)-N(6) = 2.241 (2.210(3)), Re(1)-Cl(1) = 2.541 (2.4657(10)); calculated (experimental) bond angles [°]: C(22)-Re(1)-N(5) = 169.88 (172.11 (13)), C(21)-Re(1)-N(6) = 170.61 (173.82(14)), C(23)-Re(1)-Cl(1) = 175.49 (176.63(11)), C(23)-Re(1)-N(6) = 94.30 (92.56(13)), C(23)-Re(1)-N(5) = 94.52 (93.70(13)), N(5)-Re(1)-N(6) = 74.05 (74.83(11)).

[24] M.E. Casida, in: J.M. Seminario (Ed.), Recent developments and applications in modern density functional theory, Theoretical and Computational Chemistry, Vol. 4, Elsevier, Amsterdam, 1996.

[25] (a) M.T. Cances, B. Mennucci, J. Tomasi, J. Chem. Phys. 107 (1997) 3032;
(b) M. Cossi, V. Barone, B. Mennucci, J. Tomasi, Chem. Phys. Lett. 286 (1998) 253;
(c) B. Mennucci, J. Tomasi, J. Chem. Phys. 106 (1997) 5151;
(d) M. Cossi, G. Scalmani, N. Rega, V. Barone, J. Chem. Phys. 117 (2002) 43.

[26] The quantum yield was calculated using the following reference. StephensonK.A. , et al., J. Am. Chem. Soc. 126 (2004) 8598.

[27] (a) A. Bourkoula, M. Paravatou-Petsotas, A. Papadopoulos, I. Santos, H.-J. Pietsch, E. Livaniou, M. Pelecanou, M. Papadopoulos, Eur. J. Med. Chem. 44 (2009) 4021;
(b) R. Alberto, R. Schibli, P.A. Schubiger, U. Abram, H.-J. Pietzsch, B. Johannsen, J. Am. Chem. Soc. 121 (1999) 6076;
(c) S. Mundwiler, M. Kundig, K. Ortner, R. Alberto, Dalton Trans. (2004) 1320.

[28] C. Fernandes, J.D.G. Correia, L. Gano, I. Santos, S. Seifert, R. Syhre, R. Bergmann, H. Spies, Bioconjug. Chem. 16 (2005) 660.