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A new tricarbonyl *fac*-[M(acac)(isc)$(CO)_3$] complex (M = Re, ^{99m}Tc) with acetylacetonate (acac) and isocyanide (isc) in a 2+1 combination

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ABSTRACT

The synthesis and characterization of the neutral 2+1 mixed ligand complex *fac*-Re$(CO)_3$(acac)(isc) (**4**) with acetylacetonate (acac) as the bidentate ligand and an isocyanide (the isocyanocyclohexane, isc) as the monodentate ligand is described. The synthesis of **4** proceeds through the intermediate formation of the *fac*-Re(acac)$(H_2O)(CO)_3$ precursor complex **2**. Complex **4** was characterized by elemental analysis, spectroscopic methods, and X-ray crystallography showing a distorted octahedral arrangement of the ligands around Re. At technetium-99m level, the corresponding *fac*-^{99m}Tc(acac)(isc)$(CO)_3$ complex **5** was obtained in high yield by reacting the *fac*-^{99m}Tc(acac)$(H_2O)(CO)_3$ precursor complex **3** with isocyanocyclohexane and its structure was established by chromatographic comparison with the prototypic rhenium complex using high performance liquid chromatography.

1. Introduction

The introduction of the air-stable *fac*-$[M(CO)_3(H_2O)_3]^+$ (M = ^{99m}Tc or Re) synthon produced by the gentle reduction of M(VII) to M(I) in aqueous medium under 1 atm of CO established the tricarbonyl *fac*-$[M(CO)_3]^+$ core as an easily accessible platform towards the synthesis of new radiopharmaceuticals labelled with Tc-99 m (for diagnosis) or Re-188 (for therapy) [1,2]. In the *fac*-$[M(CO)_3(H_2O)_3]^+$ synthon three coordination sites are occupied by CO groups in the stable *fac*-configuration while the remaining three coordination sites are occupied by water molecules that can be easily replaced by a great variety of ligands, or ligand combinations [3].

The 2+1 mixed ligand system, combining a bidentate and a monodentate ligand, has been successfully applied to the *fac*-$[M(CO)_3(H_2O)_3]^+$ synthon [4] leading to stable tricarbonyl complexes with a variety of donor atom groups [5–8]. In principle, both the monodentate and the bidentate ligand can be tethered to a biomolecule rendering the 2+1 combination a versatile system suitable for the synthesis of radiopharmaceuticals with desired properties in terms of target tissue specificity, pharmacokinetic behavior and labeling yield [5,7,8].

Our interest in new ligand combinations for the tricarbonyl *fac*-$[M(CO)_3]^+$ core for potential applications have led us to investigate the acetylacetone/isocyanide 2+1 combination. Acetylacetone (**1**) is a well-established bidentate ligand that coordinates to transition metals through the acetylacetonate (acac) anion [9] and can be synthetically modified to incorporate a targeting biomolecule at carbon C-2 and at the edge carbons C-4/C-5 (Fig. 1) [10]. Complexes of **1** with rhenium and technetium at various oxidation states have been reported [6,11] and recently Benny et al. described the synthesis of the 2+1 tricarbonyl Re(acac)(pyridine)$(CO)_3$, proceeding through the intermediate formation of Re(acac)$(H_2O)(CO)_3$ (**2**) [12]. On the other hand, the isocyanide (isc) is a strong, amenable to derivatization, monodentate ligand often used in technetium and rhenium chemistry [4–7,13], its most acclaimed derivative being ^{99m}Tc(I)-MIBI, the myocardial imaging radiopharmaceutical in clinical practice bearing six isocyanide ligands in its coordination sphere.

We present herein the synthesis and characterization of the mixed ligand complex *fac*-Re(acac)(isc)$(CO)_3$ (**4**) where isocyanocyclohexane was employed as a representative isocyanide ligand. Complex **4** was isolated in high yield and was characterized by elemental analysis, spectroscopic methods and X-ray analysis. At technetium-99m level, the corresponding *fac*-^{99m}Tc(acac)(isc)$(CO)_3$ complex **5** was also obtained in high yield.

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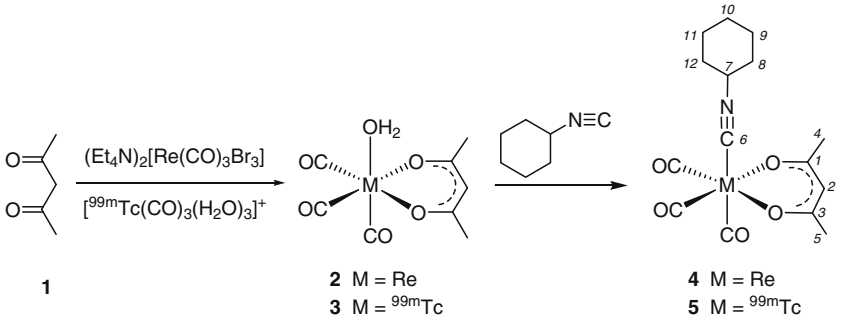

Fig. 1. Synthetic scheme for complexes **4** and **5**.

2. Experimental

2.1. Materials and methods

All reagents and organic solvents used in this study were purchased from Aldrich and used without further purification. Solvents for high-performance liquid chromatography (HPLC) were HPLC-grade. They were filtered through membrane filters (0.22 μm, Millipore, Milford, MA) and degassed by a helium flux before and during use. $[NEt_4]_2[ReBr_3(CO)_3]$ was prepared according to published procedure [14]. For ^{99m}Tc labeling, a kit containing 5.5 mg $NaBH_4$, 4 mg Na_2CO_3 and 10 mg Na-K tartarate, was purged with CO gas prior to addition of $Na^{99m}TcO_4$, as described in the literature [1].

IR spectra were recorded as KBr pellets on a Perkin–Elmer 1600 FT-IR spectrophotometer in the region 4000–500 cm^{-1}. The NMR spectra were recorded in DMSO-d_6 at 25 °C on a Bruker 500 MHz Avance DRX spectrometer using $(CH_3)_4$ Si as the internal reference. Elemental analysis for C, H and N was conducted on a Perkin–Elmer 2400 automatic elemental analyzer. HPLC analysis was performed on a Waters 600 chromatography system coupled to both a Waters 2487 Dual λ Absorbance detector and a Gabi gamma detector from Raytest. Separations were achieved on a C-18 RP (25.4 cm × 2.5 cm, 5 μm porosity) column eluted with a binary gradient system at a 1 mL/min flow rate. Mobile phase A was methanol containing 0.1% trifluoroacetic acid, while mobile phase B was water containing 0.1% trifluoroacetic acid. The elution gradient was 0–1 min 100% B (0% A), followed by a linear gradient to 90% A (10% B) in 9 min; this composition was held for another 15 min. After a column wash with 95% A for 5 min, the column was re-equilibrated by applying the initial conditions (100% B) for 15 min prior to the next injection.

2.2. Synthesis of the Re(acac)(isc)$(CO)_3$, complex **4**

Complex **4** was synthesized through the intermediate formation of Re(acac)$(H_2O)(CO)_3$ (**2**) according to a published procedure [12] with slight modifications. Briefly, to the solution of 2,4-acetylacetone (1.0 mmol) in 8 mL water (pH 6, by the addition of small aliquots of a 0.1 N sodium bicarbonate solution) 0.6 mmol of $[NEt_4]_2[ReBr_3(CO)_3]$ were added. The solution was heated to 85 °C for 4 hours to yield **2** as a yellowish precipitate that was filtered and washed with water. Yield 50%. HPLC: t_R = 14.1 min.

To a stirred solution of **2** (40 mg, 0.1 mmol) in 10 mL methanol, isocyanocyclohexane (isc, 11 mg, 0.1 mmol) in 2 mL methanol was added. The solution was stirred for 3 h and the reaction progress was monitored by HPLC. Subsequently, the solvent was removed under reduced pressure and the product was dried at high vacuum to give complex **4** in a yield of 46 mg (98%). Crystals suitable for X-ray analysis were obtained by recrystallization from dichloromethane/hexane.

HPLC: t_R = 16.3 min, I.R. (KBr, cm^{-1}): 2212, 2026, 1946, 1911; *Anal.* Calc. for $C_{15}H_{18}NO_5Re$: C, 37.65; H, 3.79; N, 2.93. Found: C, 37.29; H, 3.75; N, 2.63%. ^{1}H and ^{13}C NMR data are given in Table 2.

2.3. Single-crystal X-ray crystallography

Crystals of **4** suitable for X-ray analysis were mounted in air on a Crystal Logic Dual Goniometer diffractometer using graphite monochromated Mo Kα radiation. Unit cell dimensions were determined by using the angular settings of 25 automatically centered reflections in the range $11 < 2\theta < 23°$ and they appear in Table 1. Intensity data were recorded using a θ–2θ scan. Three standard reflections monitored every 97 reflections showed less than 3% variation and no decay. Lorentz, polarization and psi-scan absorption corrections were applied using Crystal Logic software. The structures were solved by direct methods using SHELXS-97 [15] and refined by full-matrix least squares techniques on F^2 using SHELXL-97 [16]. Further crystallographic details of **4**: $2\theta_{max} = 50°$, scan speed 2.5°/min, scan range $1.6 + \alpha_1\alpha_2$ separation, reflections collected/unique/used 3043/2901 [R_{int} = 0.0206]/2901, 250 parameters refined, $[\Delta\rho]_{max}/[\Delta\rho]_{min}$ = 1.499/−1.088 e/Å^3, $[\Delta/\sigma]_{max}$ = 0.007, R_1/wR_2 (for all data) = 0.0306/0.0756. Hydrogen atoms were located by difference maps and were refined isotropically, except those of the methyl groups which were introduced at calculated positions as riding on bonded atoms. All non-H atoms were refined anisotropically.

2.4. Synthesis of ^{99m}Tc(acac)(isc)$(CO)_3$ complex **5**

Four hundred micro litres of a freshly prepared solution of the *fac*-$[^{99m}Tc(CO)_3(H_2O)_3]^+$ precursor (pH 6) were added to a vial containing a 600 μL solution of acetylacetone (2 mg) in water. The vial was sealed, flushed with N_2 and heated for 15 min at 80 °C. HPLC analysis demonstrated the formation of a single complex (radiochemical yield > 90%) assigned to *fac*-^{99m}Tc(acac)$(H_2O)(CO)_3$ complex **3** by comparative HPLC studies using a sample of the *fac*-Re(acac)$(H_2O)(CO)_3$ complex **2** as reference (Fig. 3). To the isolated by HPLC solution (2 mL) of the *fac*-^{99m}Tc(acac)$(H_2O)(CO)_3$ complex **3**, 1 mg of isocyanocyclohexane was added (concentration of isc in the reaction mixture was 4.6×10^{-3} M) and the mixture was left at room temperature for 30 min. HPLC analysis of the reaction mixture demonstrated the formation of a single complex (radiochemical yield > 98%). The yield of the reaction remained quantitative (95%) at concentrations of isc down to 1×10^{-3} M, while at isc concentration of 2.5×10^{-4} M the yield decreased to approx. 80%. The identity of the ^{99m}Tc complex **5** was assigned by comparative HPLC studies using samples of the well characterized *fac*-Re(acac)(isc)$(CO)_3$ complex **4** as reference (Fig. 3). The radioactivity recovery of

Table 1
Summary of crystal, intensity collection and refinement data for complex **4**.

Formula	$C_{15}H_{18}NO_5Re$
Formula weight	478.50
T (K)	298
λ (Å)	Mo Kα 0.710730
Space group	$P\bar{1}$
a (Å)	9.158(5)
b (Å)	9.754(5)
c (Å)	10.930(5)
α (°)	100.30(2)
β (°)	103.99(2)
γ (°)	110.83(2)
V (Å^3)	846.9(7)
Z	2
D_{Calc} (Mg m^{-3})	1.876
Absorption coefficient μ (mm^{-1})	7.195
F (0 0 0)	460
Goodness-of-fit (GOF) on F^2	1.136
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0287$[a], w$R_2 = 0.0743$[a]

[a] For 2775 reflections with $I > 2\sigma(I)$.

Table 2
^{1}H and ^{13}C NMR chemical shifts (ppm) for complex **4** in DMSO-d_6 at 25 °C. The numbering of the atoms is shown in Fig. 1.

		C-1, C-3	188.74
H-2	5.56	C-2	101.95
H-4, H-5	1.94	C-4, C-5	27.03
		C-6	140.96 $J_{^{14}N-^{13}C}$ = ±16.3 Hz[a]
H-7	4.26	C-7	53.70
H-8, H-12	1.76, 1.69	C-8, C-12	30.86
H-9, H-11	1.47	C-9, C-11	21.17
H-10	1.45, 1.35	C-10	24.22
		C≡O	193.34, 193.18

[a] The $J_{^{14}N-^{13}C}$ was directly measurable from the 1D ^{13}C spectrum of complex **4**.

the HPLC column after the injections was monitored and found to be quantitative.

3. Results and discussion

3.1. Synthesis and characterization of fac-Re(acac)(isc)(CO)$_3$ 4

Isocyanocyclohexane acts as monodentate ligand and reacts readily with the *fac*-Re(acac)(H_2O)(CO)$_3$ precursor complex **2** in methanol to generate the corresponding neutral *fac*-Re(acac)(isc)(-CO)$_3$ complex **4** (Fig. 1). HPLC analysis of the reaction mixture showed the formation of a single product in excellent yield. Complex **4** was collected as yellowish solid and characterized by elemental analysis, spectroscopic methods and X-ray crystallography. It is soluble in methanol, acetone, dichloromethane and insoluble in *n*-hexane and water. It is stable in the solid state and in solution for months as shown by HPLC and NMR. The infrared spectra of complex **1** demonstrate strong bands at 2026, 1946 and 1911 cm^{-1} attributed to the C≡O stretch of the *fac*-[Re(CO)$_3$]$^+$ unit [17] and a sharp resonance at 2212 cm^{-1} attributed to the N≡C stretch.

The ^{1}H and ^{13}C NMR chemical shifts for complex **4** are given in Table 2 and its ^{1}H–^{13}C correlation spectrum is shown in Fig. 4. The chemical shifts of the C-2 proton and carbon as well as those of the C-4 and C-5 methyl groups of the acac moiety correspond (within 0.1 ppm for the ^{1}H and 1.5 ppm for the ^{13}C) to the chemical shifts obtained for the enol tautomer of plain acetylacetone in DMSO-d_6 ([18] and our data]. These data are consistent with coordination of the acetylacetonate anion to the rhenium core and formation of a six-membered cyclic enol-like form.

In the isocyanide ligand downfield shifts are noted for the H-7 proton (0.5 ppm) and C-7 carbon (2.8 ppm) upon coordination compared to the free isocyanocyclohexane in DMSO-d_6 ([19] and our data), while the rest of the protons and carbons of the cyclohexane moiety are affected to a much lesser degree. The C-6 isocyanide carbon is shifted upfield by 13.4 ppm by coordination; apparently, delocalization of the partial negative charge on C-6 through resonance hybrid structures is greatly reduced upon metal binding, resulting in increased shielding. The increase of the contribution of the –N≡C: resonance hybrid upon metal binding may be also reflected in the increase of the $J_{^{14}N-^{13}C}$ coupling constant from ±4.8 Hz in the free isocyanocyclohexane to ±16.3 Hz in complex **4**, in accordance with the increase of J with increasing s character of the bond between the coupled nuclei [20].

3.2. Description of the structure

An ORTEP diagram of complex **4** is given in Fig. 2 and selected bond distances and angles are listed in Table 3. The distorted octahedral environment of the Re atom in the structure of **4** is defined by the three facially bound CO groups, the nitrilo ligand and the oxygen atoms of the acac$^-$. The Re-carbonyl bond distances, 1.906(6)–1.963(6) Å, are consistent which those found in other Re-tricarbonyl complexes [21,12] and substantially shorter than the Re–C7 bond length (2.094(6) Å). The Re–acac bond distances are the larger in the coordination sphere at 2.138(4) and 2.145(4) Å. The six-membered ring in the coordination sphere is almost planar with C13 being ~0.13 Å out of the best mean plane of the six atoms. The six-membered ring of the nitrilo ligand adopts the stable chair conformation with C1 and C4 being 0.62 and 0.66 Å out of the mean plane of the remaining four atoms.

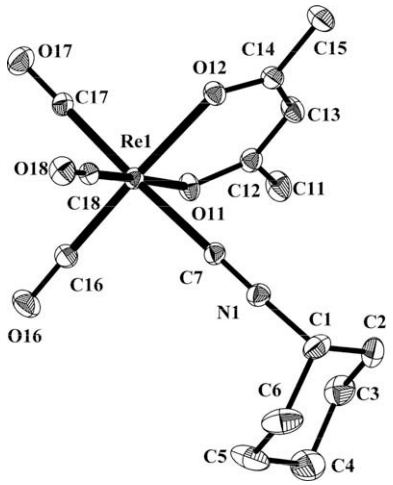

Fig. 2. Labeled ORTEP plot of complex **4** with ellipsoids drawn at the 30% probability level. Hydrogen atoms have been omitted for clarity.

3.3. Synthesis of technetium-99m complex

At technetium-99 m level, the complex *fac*-[^{99m}Tc(acac)(isc)(-CO)$_3$] (**5**) was obtained quantitatively (>95%) by reacting the *fac*-[^{99m}Tc(acac)(H_2O)(CO)$_3$] precursor complex **3** at room temperature with isocyanocyclohexane. The reaction mixture was analyzed by HPLC and the analysis demonstrated that the reaction produces a single complex. The identity of complex **2** was established by HPLC comparison of its retention time to that of the analogous well-characterized rhenium complex, **1** by applying parallel radiometric and photometric detection (Fig. 3).

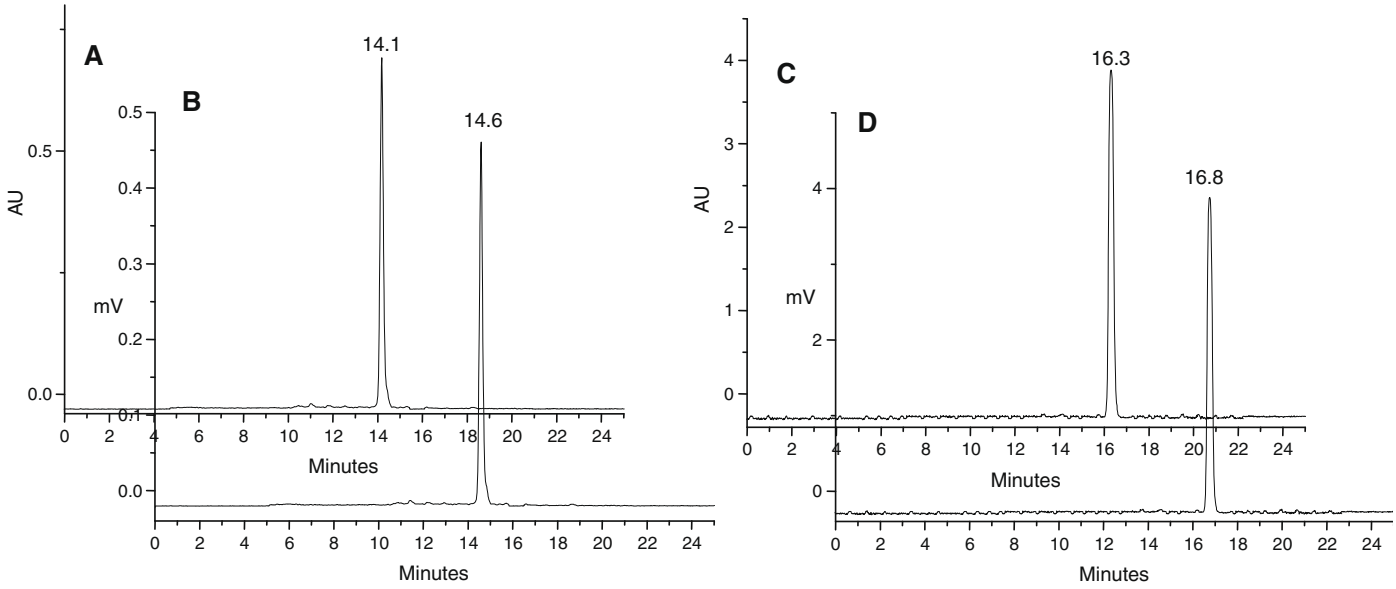

Fig. 3. Comparative reverse-phase HPLC chromatograms: (A, C): UV recording at 254 nm, *fac*-Re(acac)(H_2O)(CO)$_3$ (**2**) and *fac*-Re(acac)(is)(CO)$_3$ (**4**), retention time: 14.1 and 16.3 min, respectively; (B, D): radiometric detection, *fac*-^{99m}Tc(acac)(H_2O)(CO)$_3$ (**3**) and *fac*-^{99m}Tc(acac)(H_2O)(CO)$_3$ (**5**), retention time: 14.6 and 16.8 min, respectively.

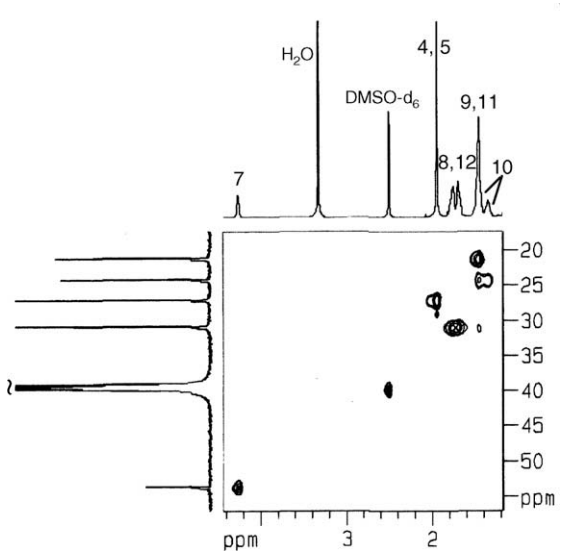

Fig. 4. ^{1}H–^{13}C correlation spectrum (HSQC, range δ_H 4.5–1.2, range δ_C 57.1–17.0) of complex **4** in DMSO-d_6 at 25 °C. The numbering of protons is shown in Fig. 1.

Table 3
Selected bond distances (Å) and angles (°) for complex **4**.

Distances			
Re(1)–C(16)	1.906(6)	Re(1)–C(7)	2.094(6)
Re(1)–C(18)	1.910(6)	Re(1)–O(11)	2.138(4)
Re(1)–C(17)	1.963(6)	Re(1)–O(12)	2.145(4)
Angles			
C(16)–Re(1)–C(18)	87.5(2)	C(17)–Re(1)–O(11)	93.5(2)
C(16)–Re(1)–C(17)	90.6(3)	C(7)–Re(1)–O(11)	84.8(2)
C(18)–Re(1)–C(17)	89.5(2)	C(16)–Re(1)–O(12)	177.1(2)
C(16)–Re(1)–C(7)	91.9(2)	C(18)–Re(1)–O(12)	94.9(2)
C(18)–Re(1)–C(7)	92.2(2)	C(17)–Re(1)–O(12)	91.0(2)
C(17)–Re(1)–C(7)	177.0(2)	C(7)–Re(1)–O(12)	86.4(2)
C(16)–Re(1)–O(11)	93.0(2)	O(11)–Re(1)–O(12)	84.5(2)
C(18)–Re(1)–O(11)	176.9(2)		

4. Conclusions

The replacement of the H_2O ligand in the *fac*-M(acac)(H_2O)(CO)$_3$ precursor complex (M = Re, 99m-Tc) by isocyanocyclohexane proceeds quickly at room temperature to generate a stable neutral complex both at rhenium and at technetium-99m level. The almost quantitative yield indicates the high affinity of the isocyanide ligand for the tricarbonyl core, and renders the system worth of further exploration through the employment of suitably derivatized pharmacophoric ligands aiming at target specific complexes.

Appendix A. Supplementary material

CCDC 750146 contains the supplementary crystallographic data for complex **4**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2010.01.004.

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