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Induced *fac-mer* rearrangements in $\{M(\text{CO})_3\}^+$ complexes ($M = \text{Re}, {}^{99\text{m}}\text{Tc}$) by a PNP ligand†Manuel Luca Besmer, * Flurina Schwitter, Federica Battistin,  ‡
Henrik Braband,  Thomas Fox, Bernhard Spingler  and Roger Alberto 

The *fac-mer* rearrangements in $[\text{MX}_3(\text{CO})_3]^{2-}$ ($M = \text{Re}, {}^{99}\text{Tc}$) induced by a pincer-type ligand (PNP) and a “halide scavenger” are reported. The reactions of $\text{fac-}[\text{}^{99\text{m}}\text{Tc}(\text{CO})_3(\text{OH})_2]_3^+$ or $[\text{}^{99\text{m}}\text{TcO}_4]^-$ in saline both yield $\text{mer-}[\text{}^{99\text{m}}\text{Tc}(\text{PNP})(\text{CO})_3]^+$, the first example of a $\text{mer-}\{\text{}^{99\text{m}}\text{Tc}(\text{CO})_3\}^+$ type complex. In contrast, reactions with terpyridine (terpy) only gave the facial κ^2 -terpy complexes with Re and ${}^{99}\text{Tc}$.

Transition metal carbonyl complexes form a large class of compounds with multiple applications.¹ The CO ligand is electronically flexible and tolerates a range of metal oxidation states. Its π -accepting ability stabilises metals in low oxidation states in particular. In the manganese triad, Re and Tc, form highly stable *fac*- $\{M(\text{CO})_3\}^+$ -based complexes. First examples for the study of such tricarbonyl complexes were reported nearly sixty years ago.² A convenient synthesis of $(\text{NEt}_4)_2[\text{ReBr}_3(\text{CO})_3]$ was published in 1994,³ the synthesis of its homologue ${}^{99}\text{Tc}$ (half-life $\sim 2 \times 10^5$ years, β^- decay $E_{\text{max}} = 293$ keV) was reported shortly thereafter starting from $(\text{NBu}_4)[\text{TcO}_4]$.⁴ Commercial interest induced an elegant pathway to $[\text{}^{99\text{m}}\text{Tc}(\text{CO})_3(\text{OH})_2]_3^+$ in aqueous media, available as a kit (Isolink® Kit).^{5,6} Access to $[\text{}^{99\text{m}}\text{Tc}(\text{CO})_3(\text{OH})_2]_3^+$ triggered a plethora of compounds with mono-, bi- or tridentate ligands towards the goal of new radiopharmaceuticals.^{7,8}

The remarkable stability of the *fac*- $\{\text{}^{99\text{m}}\text{Tc}(\text{CO})_3\}^+$ motif and its capability to coordinate readily a wide range of ligands led to many compounds with Re and ${}^{99}\text{Tc}$. In turn, the meridional isomer (*mer*- $\{M(\text{CO})_3\}^+$) has not been in the focus of ${}^{99\text{m}}\text{Tc}$ research since it is not accessible along a facile pathway. For Re(I), a few examples of *mer*- $\{\text{Re}(\text{CO})_3\}^+$ -type complexes have been reported,^{9,10} amongst which Langer *et al.* presented the

light induced *fac-mer* rearrangement of a carbodiphosphorane complex.¹¹ One of the first *mer*- $\{\text{Tc}(\text{CO})_3\}^+$ complexes was obtained from $[\text{TcOCl}_4]^-$ with PPh_3 under a CO atmosphere.¹² Intramolecular isomerisation has in fact been observed recently upon coordination of sterically highly demanding isonitrile ligands¹³ and a variety of *mer*- $\{\text{Tc}(\text{CO})_3\}^+$ -type complexes have been reported based on the *mer*- $[\text{Tc}(\text{CO})_3(\text{OH})_2(\text{PPh}_3)_2]^+$ starting material.^{14,15}

In an attempt to explore scarce *fac-mer* isomerisations for Re and Tc tricarbonyl complexes, we chose pincer-type ligands.¹⁶ The desired *mer* arrangement in the complexes refers solely to three carbonyl ligands, rather than three monodentate ligands of which some are carbonyl ligands or the meridional coordination of the pincer ligand. These tridentate PNP-based pincer systems are preorganised for meridional coordination with various d-elements, also with ${}^{99}\text{Tc}$, as recently reported by us.^{17,18} The distinct preference of pincer ligands such as 2,6-bis((di-tertbutylphosphino) methyl)pyridine (${}^{\text{Pyr}}\text{PNP}^{\text{tBu}}$) for coordinating the metal centre in a meridional fashion prompted us to explore their interactions with Re and ${}^{99\text{m}}\text{Tc}$ tricarbonyl cores. Of special interest was the question if the *mer*- $\{\text{}^{99\text{m}}\text{Tc}(\text{CO})_3\}^+$ motif was accessible for radiopharmaceuticals as well.

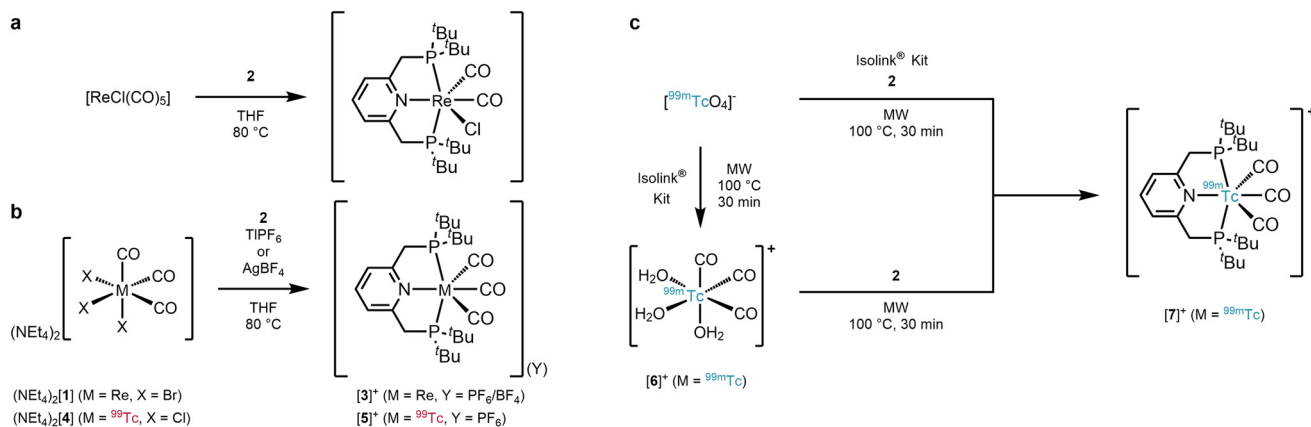
The reaction of ${}^{\text{Pyr}}\text{PNP}^{\text{tBu}}$ (2) with *e.g.* $[\text{ReCl}(\text{CO})_5]$ in refluxing THF yields *cis*- $[\text{Re}({}^{\text{Pyr}}\text{PNP}^{\text{tBu}})(\text{CO})_2\text{Cl}]$ after loss of three CO's (Scheme 1a).¹⁹ When starting from *fac*- $[\text{ReBr}_3(\text{CO})_3]^{2-}$ (*fac*-[1]²⁻) for inducing a *fac-mer* rearrangement, heating of *fac*-[1]²⁻ with 2 in THF gave the expected yellowish product *cis*- $[\text{Re}({}^{\text{Pyr}}\text{PNP}^{\text{tBu}})(\text{CO})_2\text{Br}]$ after loss of two Br^- and one CO ligand. Obviously, cleavage of a 3rd halide from *fac*-[1]²⁻ and CO rearrangement is disfavoured over dissociation of one CO. Conceptually, we hypothesised that a “halide scavenger” would change this preference, facilitate halide removal and lead to the desired rearrangement. Indeed, performing the reaction of *fac*-[1]²⁻ with 2 in THF (80 °C, 81 h) and with 3 equiv. of TiPF_6 gave the rearrangement to *mer*- $[\text{Re}({}^{\text{Pyr}}\text{PNP}^{\text{tBu}})(\text{CO})_3](\text{PF}_6)$ (*mer*-[3](PF₆)) in 34% yield (Scheme 1b). The spectroscopic analysis of *mer*-[3](PF₆) displayed the expected symmetric signals in the

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Scheme 1 a) Synthesis of *fac*-[Re(^{Pyrr}PNP^{tBu})(CO)₂Cl] from [ReCl(CO)₃];¹⁹ (b) syntheses of *mer*-[M(^{Pyrr}PNP^{tBu})(CO)₃]⁺ (*mer*-[3](BF₄ or PF₆) and *mer*-[5](PF₆) by reaction of *fac*-[1]²⁻ or *fac*-[4]²⁻ with ^{Pyrr}PNP^{tBu} (**2**) in presence of TIPF₆ (3 equiv.) and/or AgBF₄ (3 equiv.); (c) synthetic pathways towards *mer*-[^{99m}Tc(^{Pyrr}PNP^{tBu})(CO)₃]⁺ (*mer*-[7]⁺) in one step (top) or two steps via *fac*-[6]⁺ (bottom). MW refers to "microwave reactor".

¹H-, ¹³C{¹H}- and ³¹P{¹H} NMR spectra (ESI Fig. S2–S4[†]). The carbon signals of the *mer*-[Re(CO)₃]⁺ moiety appear as two triplets at δ 197.3 (²J_{P-C} = 7.8 Hz) and 196.5 ppm (²J_{P-C} = 3.6 Hz). For the PF₆⁻ anion a doublet at δ -72.9 ppm (¹J_{F-P} = 710.8 Hz) was found in the ¹⁹F NMR spectrum and a septet at δ -144.4 ppm (¹J_{P-F} = 710.8 Hz) in the ³¹P{¹H} NMR spectrum. The IR spectrum (KBr pellet) of *mer*-[3](PF₆) displayed a set of three bands ν_{CO} at 2047, 1946 and 1913 cm⁻¹ in a ratio of 1 : 2 : 2. The observed pattern coincides with a *mer*-{Re(CO)₃}⁺ moiety and differs distinctly from the characteristic facial starting material ((NEt₄)₂[1]: 2000 and 1867 cm⁻¹). A single crystal analysis confirmed *mer*-[Re(^{Pyrr}PNP^{tBu})(CO)₃](PF₆) (Fig. 1, top). The analogous reaction with AgBF₄ (instead of TIPF₆) yielded *mer*-[3](BF₄). Mechanistically, we hypothesise that the pincer ligand initially coordinates in a bidentate fashion forming the intermediate *fac*-[ReBr(^{Pyrr}PNP^{tBu})(CO)₃], which has been observed in UHPLC-ESI-MS. Upon abstraction/dissociation of the third halide ligand, the isomerisation takes place with concomitant tridentate pincer coordination. Following these results of an intramolecular *fac*-*mer* rearrangement, the homologous ⁹⁹Tc reaction was performed. The technetium complex *fac*-[4]²⁻ reacted with **2** in THF (80 °C, 5 h) in the presence of 3 equiv. of TIPF₆ straight to *mer*-[Tc(^{Pyrr}PNP^{tBu})(CO)₃](PF₆) (*mer*-[5](PF₆)) in 27% yield as an off-white crystalline solid. The spectroscopic analysis revealed analogous features as compared to *mer*-[3](PF₆) with a broad ⁹⁹Tc NMR signal at δ -1574 ppm (Δ₃ = 2.2 kHz). As in *mer*-[3]⁺, the IR spectrum evidences a *mer*-[Tc(CO)₃]⁺-moiety with three bands ν_{CO} at 2053, 1960 and 1923 cm⁻¹, only shifted slightly as compared to its rhenium congener. The solid-state structure of (*mer*-[5](PF₆)) (Fig. 1, bottom) finally confirms structurally the rearrangement from *fac*-[Tc(CO)₃]⁺ in *fac*-[4]²⁻ to *mer*-[Tc(CO)₃]⁺ in *mer*-[5]⁺. The products of these isomerisations with the ^{Pyrr}PNP^{tBu} ligand add to the limited number of examples for meridional tricarbonyl complexes. We hypothesise that the strong preference for planar binding and the rather bulky phosphine substituents of the pincer, similar to the reported isonitrile study,¹³ induce an intramolecular rearrangement.

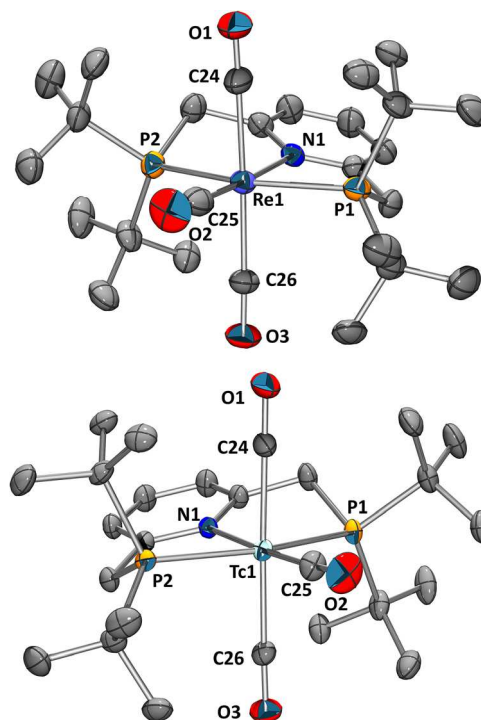


Fig. 1 Ellipsoid displacement plots²⁰ of *mer*-[Re(^{Pyrr}PNP^{tBu})(CO)₃](PF₆) ([3](PF₆), top) and *mer*-[Tc(^{Pyrr}PNP^{tBu})(CO)₃](PF₆) ([5](PF₆), bottom). Ellipsoids represent a 35% probability. Hydrogen atoms and counterions have been omitted for clarity.

Having established the macroscopic reactions in organic solvents with Re and ⁹⁹Tc, the question arose if a similar pathway was accessible for ^{99m}Tc in aqueous saline (0.9% NaCl) media. In an ideal case, the labelling of the pincer ligand requires a short reaction time and forms the product in high yield and radiochemical purity (RCP). In a first approach, *fac*-[^{99m}Tc(CO)₃(OH₂)₃]⁺ (*fac*-[6]⁺) was prepared with the Isolink® Kit in the microwave reactor within 30 min at 100 °C. The aqueous solution containing *fac*-[6]⁺ was degassed



(to remove CO), a solution of $\text{Py}^{\text{r}}\text{PNP}^{\text{tBu}}$ in EtOH (degassed) was added and the mixture heated in a microwave reactor for 30 min at 100 °C (1 : 1 H₂O/EtOH). The radio-HPLC analysis of the product solution showed one main product peak at 25.5 min (92% RCP). Coinjection of a purified sample with the previously obtained *mer*-[5](PF₆) confirmed the identity of the only product as *mer*-[^{99m}Tc($\text{Py}^{\text{r}}\text{PNP}^{\text{tBu}}$)(CO)₃]⁺ (Fig. 2, the separation of about 1.5 min corresponds to the separation of the UV/vis- and γ -detector). To the best of our knowledge, this is the first example of a *mer*-[^{99m}Tc(CO)₃]⁺-type complex. For practical purposes, a one-step preparation is preferable over the two-step synthesis described above. For this purpose, the saline [^{99m}TcO₄]⁻ eluate was degassed and mixed with the boranocarbonate (Na₂H₃BCO₂), tartrate (Na₂C₄H₄O₆) and tetraborate (Na₂B₄O₇).²¹ A degassed EtOH solution with the pincer ligand was added. After heating in the microwave reactor for 30 min at 100 °C, the solution was analysed by HPLC, showing the equivalent product peak at 25.5 min. A true one-pot preparation is therefore possible. In contrast to the macroscopic scale with Re and ⁹⁹Tc, where the challenge was the removal of three halide ligands from the starting material, the three aqua ligands are readily replaced by the tridentate pincer, which induced a *fac-mer* rearrangement. Mechanistically, we cannot exclude in the one-step procedure an initial PNP coordination in one of the oxidation states between ^{99m}Tc(VII) and ^{99m}Tc(I), followed by the coordination of the CO ligands. For the two-step approach however (*vide supra*), the reaction starts from a *fac*-{^{99m}Tc(CO)₃}⁺ unit in the presence of a large excess of Cl⁻. The final meridional product must thus be the result of an intramolecular rearrangement induced by the PNP ligand.

To assess if the *mer*-{M(CO)₃}⁺ structure can be generalised to other ligands with meridional preference, terpyridine (terpy) as a more flexible tridentate ligand is an obvious choice. Terpy commonly binds in a meridional fashion as is known from many complexes.²² Following the pathway described above, *fac*-[1]²⁻ was reacted with terpy in the presence of TlPF₆. After work-up, the analysis of the pale yellowish, crystalline material by NMR and IR indicated a κ^2 -terpy complex (Scheme 2). Three bands in the CO region ν_{CO} at 2021, 1916 and 1895 cm⁻¹ were observed, out of which the two lower energy vibrations are poorly resolved. In contrast to *mer*-

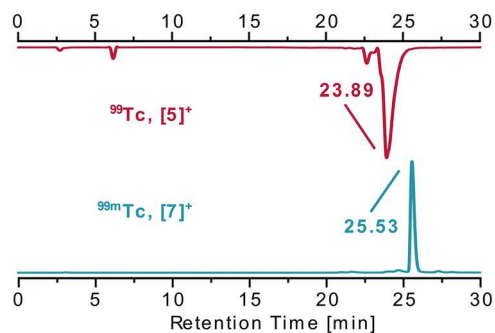
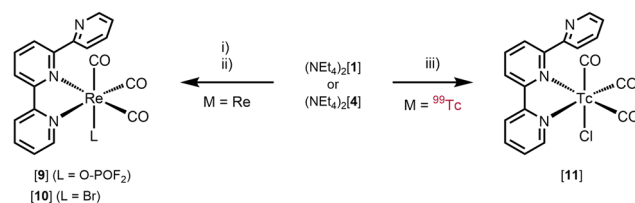


Fig. 2 HPLC traces for the coinjection of *mer*-[5]⁺ (top, UV-trace) and *mer*-[7]⁺ (bottom, γ -trace).



Scheme 2 Syntheses of *fac*-[Re(κ^2 -terpy)(CO)₃L] ([9] (L = O-POF₂), [10] (L = Br)) and *fac*-[Tc(κ^2 -terpy)(CO)₃Cl] ([11]). Conditions: (i) (NEt₄)₂[ReBr₃(CO)₃], 3 TlPF₆, terpy, THF, 80 °C, 39 h; (ii) (NEt₄)₂[ReBr₃(CO)₃], 3 AgBF₄, terpy, THF, 80 °C, 24 h; (iii) (NEt₄)₂[TcCl₃(CO)₃], terpy, MeOH, 50 °C, 4 h.

[3]⁺ and *mer*-[5]⁺ these spectral signatures are indicative for *fac*-{M(CO)₃}⁺ moieties. The ³¹P{¹H} NMR spectrum revealed a triplet at δ -16.2 ppm (¹J_{P-F} = 961.7 Hz) and in the ¹⁹F NMR spectrum a doublet at δ -83.0 ppm (¹J_{F-P} = 964.6 Hz) was found. The latter signature is not compatible with the one expected for PF₆⁻, indicating a phosphorous nuclei coupling only to two neighbouring fluorine nuclei. An X-ray diffraction analysis of single crystals allowed the identification of the product as *fac*-[Re(κ^2 -terpy)(CO)₃(PO₂F₂)] (*fac*-[9]) (Fig. 3, top). The *fac-mer* isomerisation was not induced by terpy, but an uncommon difluorophosphate (PO₂F₂⁻) anion occupied the sixth coordination site. The comparison of the recorded IR spectrum with reported values for PO₂F₂⁻ led to the identifi-

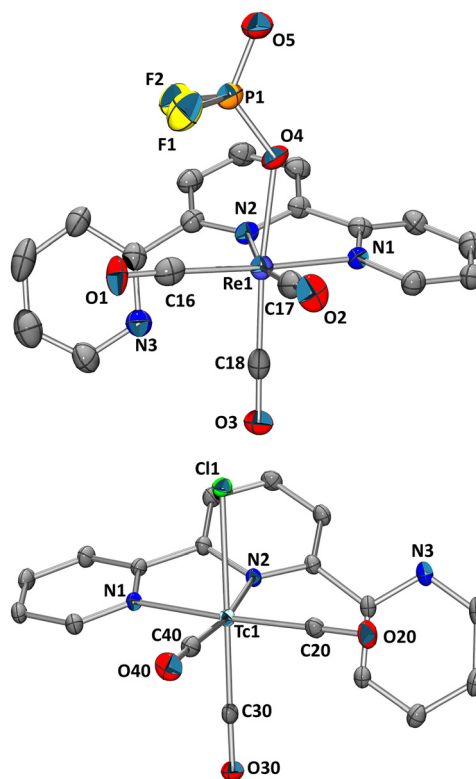


Fig. 3 Ellipsoid displacement plots²⁰ of *fac*-[Re(κ^2 -terpy)(CO)₃(PO₂F₂)] ([9], top) and *fac*-[Tc(κ^2 -terpy)(CO)₃Cl] ([11], bottom). Ellipsoids represent a 35% probability. Hydrogen atoms are omitted for clarity.



cation of characteristic bands (1313, 1158, 842 and 498 cm^{-1}).²³ The PF_6^- anion hydrolysed, probably as a result of either residual traces of water in the glassware²⁴ or a transition metal assisted pathway as observed similarly for other metals.^{25,26} The decomposition reaction was not further explored in detail and the analogous reaction with ^{99}Tc indicated the formation of a similar product. The flexibility and reduced steric demand of the terpyridine ligand, compared to PNP, is evidenced in the lack of isomerisation and the isolation of facial tricarbonyl complexes. It cannot be excluded that a thermodynamic driving force for halide substitution, while forming a M–P bond in comparison to a M–N, contributes to the different reactivities. Similar complexes with terpy have been reported starting from $[\text{ReBr}(\text{CO})_5]$ via reaction in toluene at 100 °C.^{27,28} The reaction of $\text{fac}[\text{1}]^{2-}$ with terpyridine in the presence of AgBF_4 represents thus an alternative pathway towards $\text{fac}[\text{Re}(\kappa^2\text{-terpy})\text{Br}(\text{CO})_3]$ ($\text{fac}[\text{10}]$, (Scheme 2)) (71%).^{27,28} Analogously for ^{99}Tc , the reaction of $\text{fac}[\text{4}]^{2-}$ with terpy in MeOH (no halide scavenger present) gave greenish $\text{fac}[\text{Tc}(\kappa^2\text{-terpy})\text{Cl}(\text{CO})_3]$ ($\text{fac}[\text{11}]$) (Fig. 3, bottom) in quantitative yield. In contrast to $\text{fac}[\text{9}]$, the IR spectrum shows two bands for the CO ligands ν_{CO} at 2022 and 1926 cm^{-1} with the latter broader and not fully resolved. The $\text{fac}\text{-}\{\text{M}(\text{CO})_3\}^+$ arrangement thus follows the rhenium model and is expected in the absence of halide scavengers. The ^{99}Tc NMR spectrum of complex $\text{fac}[\text{11}]$ shows a comparable sharp signal at δ –1020 ppm ($\Delta_{\frac{1}{2}} = 420$ Hz). The ^1H NMR spectrum at 298 K revealed mostly broad signals except for one sharp triplet. Performing the measurements at 235 K allowed the observation of distinct signals and multiplicities. The broadening of the signals at ambient temperature stems from fluxional behaviour of the $\kappa^2\text{-terpy}$ ligand, as has been observed with the rhenium congener (Scheme S1, ESI†).²⁷ Interestingly, the rhenium complex [9] with the uncommon (PO_2F_2^-) anion does not show any fluxional behaviour at 298 K.

We report herein one of the rare examples of an intramolecular $\text{fac}\text{-}\{\text{M}(\text{CO})_3\}^+$ to $\text{mer}\text{-}\{\text{M}(\text{CO})_3\}^+$ rearrangement with rhenium and technetium, induced by the bulky $\text{PyrPNP}^{\text{tBu}}$ pincer ligand. To enable these rearrangements with Re and ^{99}Tc ($\text{fac}[\text{1}]^{2-}$ and $\text{fac}[\text{4}]^{2-}$), concomitant halide precipitation with Ag(I) or Tl(I) is mandatory. The adaption of this chemistry from THF to saline and $^{99\text{m}}\text{Tc}$ chemistry gave a $\text{mer}\text{-}\{^{99\text{m}}\text{Tc}(\text{CO})_3\}^+$ structure for the first time. The product $\text{mer}\text{-}\{^{99\text{m}}\text{Tc}(\text{PyrPNP}^{\text{tBu}})(\text{CO})_3\}^+$ is water stable and can be made along a one- or a two-step synthesis. Large excesses of chloride do not interfere with the mer -product formation, implying the opportunity of making further $\text{mer}\text{-}\{^{99\text{m}}\text{Tc}(\text{CO})_3\}^+$ complexes, in extension to the usual $\text{fac}\text{-}\{^{99\text{m}}\text{Tc}(\text{CO})_3\}^+$ compounds. The observed reactivities with $^{99\text{m}}\text{Tc}$ thus enclose a potential to broaden the scope for tricarbonyl complexes. Potential decarbonylation in meridional tricarbonyl complexes could be exploited as a synthetic strategy for new dicarbonyl-based radiopharmaceuticals. We are currently investigating if reactivities of sterically less demanding ligands such as terpy and $^{99\text{m}}\text{Tc}$ lead to the same structures, contrasting macroscopic results described above.

Author contributions

MLB edited and wrote the manuscript, conceptualised the project and performed experiments, FS performed experiments (Re and ^{99}Tc), FB performed $^{99\text{m}}\text{Tc}$ labelling experiments, HB advised $^{99\text{m}}\text{Tc}$ experiments, TF performed low temperature NMR studies, BS advised and supervised all crystallographic data collections and refinements, RA revised the manuscript, performed ^{99}Tc experiments and initiated the project.

Conflicts of interest

There are no conflicts to declare.

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