A simple single-step synthesis of [$^{99}Tc_3H_3(CO)_{12}$] from [$^{99}TcO_4$]$^-$ and its X-ray crystal structure. Application to the production of no-carrier added [$^{188}Re_3H_3(CO)_{12}$]

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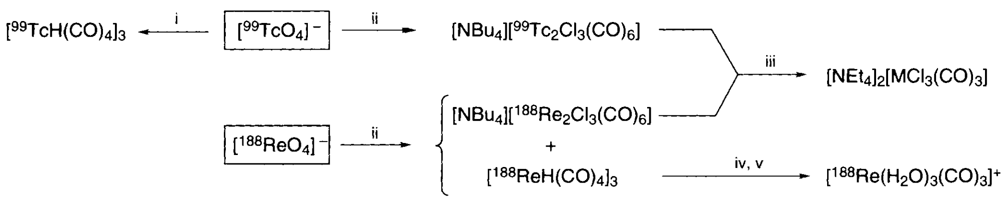
Reduction of no-carrier added [$^{188}ReO_4$]$^-$ (ng range) in thf–[NBu_4]Cl with BH_3·thf under an atmosphere of CO yields [$^{188}ReCl_3(CO)_3$]$^{2-}$ and [$^{188}Re_3(\mu\text{-}H)_3(CO)_{12}$]; under similar conditions as with [$^{188}ReO_4$]$^-$, the first μ-hydrido-bridged ^{99}Tc hydrido carbonyl complex is prepared and structurally characterised.

We have recently reported a simple one-pot synthesis of the useful M^{I} precursor complexes [NEt_4]$_2$[$MCl_3(CO)_3$] (M = Tc **1a**, Re **1b**) starting directly from [NBu_4][MO_4] under ambient conditions.[1] Dissolution of **1** in water yields the corresponding air-stable 'aqua ion' [$M(OH_2)_3(CO)_3$]$^+$ (M = ^{99}Tc **2a**, Re **2b**, ^{188}Re **2c**).[2] Technetium-99m carbonyl complexes of appropriately derivatized ligands may find applications in nuclear medicine, as recently demonstrated by the imaging of brain receptors using a technetium(v) complex.[3] **2c** can be used as a direct radiolabelling agent for proteins and applied in radioimmunotherapy.[4] The synthetic conditions for the preparation of **1a** or **1b**, as depicted in Scheme 1, are almost identical. We found that the main product is [$M_2(\mu\text{-}Cl)_3(CO)_6$]$^-$ which can, by addition of [NEt_4]Cl, be quantitatively converted into **1a** and **1b**. However, adaptation of the synthetic conditions to trace amounts of [$^{188}ReO_4$]$^-$ (37 MBq = 1 ng) revealed at least two products, as evidenced by TLC [R_f = 0.39 corresponds to **2a** with one unknown species at R_f = 0.69). The amount of the unknown species increased with the amount of BH_3·thf. Consequently, the reduction of [TcO_4]$^-$ was performed exclusively in the presence of BH_3·thf, 1 atm of CO in thf and at room temperature. TLC experiments confirmed the compound at R_f = 0.69 as the main product together with a minor amount of another species with a slightly higher R_f value. The reaction was also followed by ^{99}Tc NMR spectroscopy. Although ^{99}Tc has a nuclear spin of 9/2 and a large quadrupole moment, the nucleus has a high NMR sensitivity and gives rise to sharp lines in symmetric complexes even in dilute solutions.[5] A few minutes after completion of [TcO_4]$^-$ addition, no pertechnetate could be detected [δ [TcO_4]$^-$ ($CDCl_3$) = 0]. The main feature of the spectrum after 3–4 h was a pattern of two signals at δ −1006 ($\Delta\nu_{1/2}$ = 135 Hz) and at δ −983 ($\Delta\nu_{1/2}$ = 125 Hz) and one strong singlet at δ −2275 ($\Delta\nu_{1/2}$ = 510 Hz), remaining unchanged over an extended period of time. After quenching with water, two different compounds could be isolated by fractional crystallisation in *ca.* 95% yield with respect to technetium. The resonance at δ −2275 belonged to the main product. Furthermore, ^{1}H NMR spectroscopy revealed one sharp singlet at δ 2.17 in $CDCl_3$, a typical '$M(CO)_4$' pattern in the IR spectrum and the same chromatographic properties as the ^{188}Re by-product. An X-ray diffraction study of the ^{99}Tc compound finally confirmed the spectroscopically derived structure of [$M_3(\mu\text{-}H)_3(CO)_{12}$] (M = ^{99}Tc **3a**, Re **3b**). An ORTEP presentation is shown in Fig. 1. The Tc and H atoms alternate and form a six-membered ring. Although these bridging hydrides are close to the heavy atoms, 19 of the 24 in the asymmetric unit could be located and refined. The Tc–H bond lengths are on average 1.84 Å. Since this triangular cluster is electronically unsaturated (48 v.e.s), Tc–Tc contacts can be expected. The distance is 3.278 Å, thus slightly longer than in **3b** with 3.241(2) Å.[6] Although such hydrido carbonyl clusters are well established for Re or Mn,[7] this class of compounds is unknown for ^{99}Tc.

Compounds **3a** and **3c** were not attacked by acid but methanolic NaOH solution was, however, reported to convert **3b** readily to [$(CO)_3Re(\mu\text{-}OMe)_3Re(CO)_3$]$^-$ and this also proved to be the case for **3a** and **3c**. After degradation, acidification of these solutions yielded **1a** and **1c** quantitatively [TLC/HPLC and ^{99}Tc NMR spectroscopy (δ = −876)].

The nature of the minor by-product (10–20% yield) found in the reaction with ^{99}Tc but not with ^{188}Re has not yet been structurally characterised; ^{1}H NMR reveals two sharp singlets in $CDCl_3$ at δ 5.30 (s, 1 H) and 2.16 (s, 3 H) and the signals for one [NBu_4] cation in the correct ratio relative to the singlets. The IR spectrum shows the typical '*fac*-$M(CO)_3$' pattern. Among the numerous rhenium hydrido carbonyls, only [NBu_4][$Re_3(\mu_3\text{-}H)(\mu\text{-}H)_3(CO)_9$] **4b** would qualitatively fit with these spectroscopic data.[8] We therefore tentatively conclude that the compound may be [NBu_4][$Tc_3(\mu_3\text{-}H)(\mu\text{-}H)_3(CO)_9$] **4a**. Solvent interaction with the Tc centres in **4a**, as observed with hydridocarbonyl rhenium complexes,[9] which result in the formation of [$Tc_3(\mu_3\text{-}H)(\mu\text{-}H)_3(CO)_9(solv)$]$^-$, would explain the two other signals in the ^{99}Tc NMR spectrum.



Scheme 1 *Reagents and conditions*: i, BH_3·thf, thf, CO; ii, BH_3·thf, [NBu_4]Cl, thf, CO; iii, [NEt_4]Cl, EtOH; iv, 5 mol dm^{-3} EtOH, NaOH; v, 1 mol dm^{-3} HCl

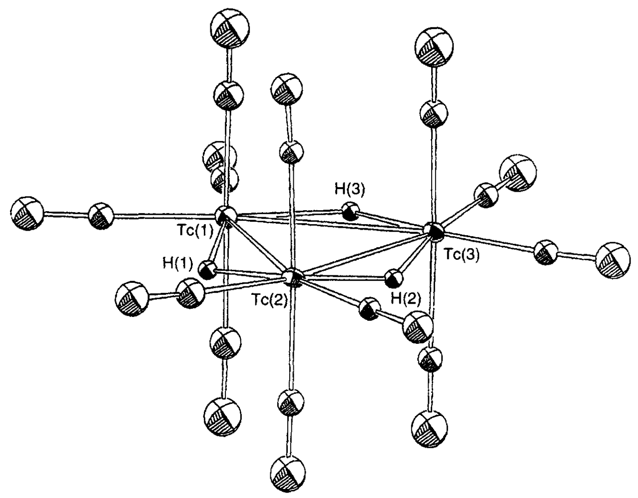


Fig. 1

^{1}H NMR data for the rhenium and technetium forms of both complexes **3** and **4** show that the signals for Tc are shifted by about 20 ppm to lower field relative to Re. In most cases, proton resonances in the α position to the coordinating atoms are found with comparable chemical shifts for Re and Tc, only for M$^\text{I}$ compounds of the formulation $[MX_2(dppe)_2]^+$ have differences as found for **3a** and **3b** been observed.[10]

Compound **3a** represents, to our knowledge, the first μ-hydrido-bridged technetium(I) compound known to date and $[HTc(CO)_5]$,[11] $[TcH(CO)(dppe)_2]$[12] and $[TcH(CO)_3(PPh_3)_2]$[13] are examples for the few terminal hydrido complexes of Tc$^\text{I}$. The convenient synthesis of **3a** furthermore represents one of the very rare examples where a tetracarbonyl complex is prepared directly from the permetalate under ambient conditions. This is particularly important in technetium chemistry, as **3a** is an alternative precursor to $[Tc_2(CO)_{10}]$. The identity of **3a** with the ^{188}Re compound **3c**, prepared on the no-carrier added level, also offers the possibility of applying organometallic hydride complexes, or derivatives thereof, in the field of nuclear medicine.

The X-ray diffraction experiment resulted in a modulated structure. The structure of $[Tc_3H_3(CO)_{12}]$ has been determined in the pseudo-monoclinic space group $C\bar{1}$ (maximal nonisomorphic subgroup of $C2/m$) with eight molecules in the asymmetric unit. Two molecules could be transferred with translation periods of about (1/4, −1/4, 0) and two molecules with (1/4, 1/4, 0) and two molecules with (1/4, 1/4, 0) to the corresponding molecules, but no further reduction to a real monoclinic space group was possible.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/73.

Footnote

† *Crystal data* for **3a**: $C_{12}H_3O_{12}Tc_3$. $M = 636.14$, monoclinic, space group $C\bar{1}$, $T = 173$ K, $a = 22.752(4)$, $b = 22.746(4)$, $c = 28.268(6)$ Å, $\beta = 92.97(1)°$, $U = 14610(5)$ Å^3, $Z = 32$, $D_c = 2.302$ g cm^{-3}, $F(000) = 9600$, graphite-monochromated Mo-Kα radiation, $\lambda = 0.71073$ Å, $\mu = 2.298$ mm^{-1}, crystal size 0.4 × 0.3 × 0.2 mm, ω-scan, $4.32 < 2\theta < 54°$, 16761 reflections collected (16725 independent, $R_{int} = 0.0152$), the structure was resolved by direct methods (SHELXS-86), all atoms were located from successive Fourier maps except four hydrogens. All atoms including the 20 localized bridging hydrides were refined by full-matrix least squares (SHELXL-93), heavy atoms anisotropic, all others isotropic, 1045 variables, $R(F) = 0.0465$, $wR(F^2) = 0.0859$.

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