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From oxo to carbonyl and arene complexes; A journey through technetium chemistry

Roger Alberto

University of Zurich, Department of Chemistry, Winterthurerstr. 190, CH-8057 Zurich, Switzerland

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Dedicated to Prof. Dr. W.A. Herrmann's 70th birthday.

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ABSTRACT

A personal note in celebration of Professor Herrmann's 70th birthday, the author describes how the successful preparation of $H_3C^{99}TcO_3$ and the still unsolved task of preparing [$Cp^{*99}TcO_3$] powered ultimately a plethora of organometallic ^{99}Tc chemistry. Driven by the need for technetium carbonyl complexes, the red wire leads from $[^{99}TcCl_3(CO)_3]^{2-}$ over the related $[^{99m}Tc(OH_2)_3(CO)_3]^+$ and $[(L^3)^{99}TcO_3]^+$ finally to $[^{99}Tc(arene)_2]^+$ complexes. It is shown how, from the fundamental search for [$Cp^{*99}TcO_3$], useful molecules for application in molecular imaging emerged.

1. Introduction

Technetium is an artificial element, located roughly in the middle of the periodic table. The question why there is at this place of the periodic system an unstable element, is rarely asked and even rarer answered in basic chemistry courses. A comprehensive explanation has recently been given by Al Sattelberger, a pioneer in the field of technetium chemistry [1]. Technetium doesn't exist on earth or, to be precise, it exists in minutest quantities only from the spontaneous fission of uranium. Due to the short half-life of all its isotopes on a geological time scale, primordial technetium decayed into its neighbouring elements, molybdenum or ruthenium. Large amounts of ^{99}Tc, enough to investigate its chemistry on the macroscopic scale, are nowadays available from the fission of ^{235}U in nuclear reactors [2]. These facts together with the question about its discovery were sufficient for me as a passionate element collector to become highly interested in technetium chemistry from the very beginning. At that time, fundamental and exciting technetium coordination or organometallic chemistry was performed by many groups worldwide but is nowadays in steep decline. The research was and still is inspired and driven by the application of the metastable ^{99m}Tc, the most widely used radionuclide in nuclear medicine [3–5]. When offered by Wolfgang Herrmann after my PhD to prepare high-valent organometallic technetium compounds I, as a coordination chemist, did not know exactly what that meant. It soon became clear however when studying a beautiful review article about rhenium he sent to me [6]. This article became pivotal since it drove me into the plethora of technetium chemistry, in high and low oxidation states. The task was clear; preparation of the lower homologues of Herrmann's famous compounds H_3C-ReO_3 and (η^5-C_5Me_5)ReO_3 (η^5-C_5Me_5 = Cp*) along the reaction schemes elaborated at that time for rhenium (Scheme 1) [7,8].

2. $^{99}Tc^{VII}$ complexes with oxo ligands

Although we learn that 4d and 5d elements are similar in their chemical behaviours, Tc and Re are not, especially in their higher oxidation states. $^{99}Tc_2O_7$ is not Re_2O_7 and H_3C-$^{99}TcO_3$ (MTcO) is not H_3C-ReO_3. After many unsuccessful attempts and repeatedly preparing highly sensitive and volatile $^{99}Tc_2O_7$, H_3C-$^{99}TcO_3$ could finally be synthesized from $^{99}Tc_2O_7$, together with $[(H_3C)_2O^{99}Tc(\mu\text{-}O)_2^{99}TcO(CH_3)_2]$, a rare example of a $^{99}Tc^{VI}$ complex [9]. The relatively small difference in oxidation potentials makes MTcO hardly

E-mail address: ariel@chem.uzh.ch.

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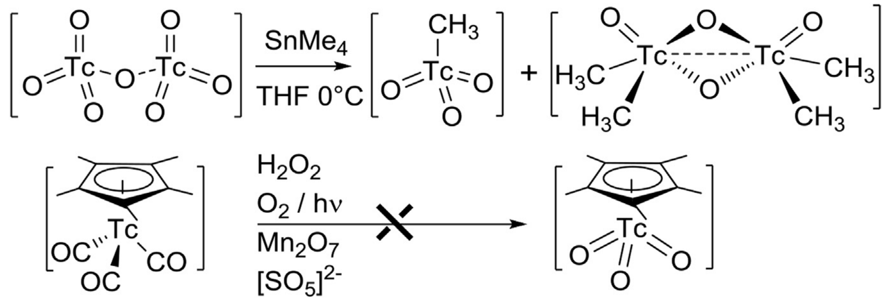


Scheme 1. High-valent organometallic ^{99}Tc complexes: Rhenium and technetium are different, all attempts to synthesize [Cp*^{99}TcO$_3$] failed, H$_3$C-^{99}TcO$_3$ is extremely volatile.

accessible, it is easily reduced to lower oxidation states. An interesting difference to its rhenium homologue is the fact that it readily adds alkenes to form the ^{99}Tc^{V}-glycolato complexes. Alan Davison, another pioneer in technetium chemistry, had previously shown that Tc^{VII} complexes of the type [(Tp)^{99}TcO$_3$] (Tp = Trofimenko type ligands) *cis*-hydroxylates alkenes to yield stable ^{99}Tc^{V}-glycolato complexes [10]. The difference is that rhenium reacts in the other direction, Re^{V}-glycolato complexes liberate alkenes when heated whereas Tc-glycolato doesn't. We used later the same procedure to directly label alkene-derivatized biomolecules with ^{99}Tc^{VII} complexes [11]. Apart from its reactivity, MTcO is highly volatile; you see the crystal and ten seconds later it is gone in the air, like dry ice.

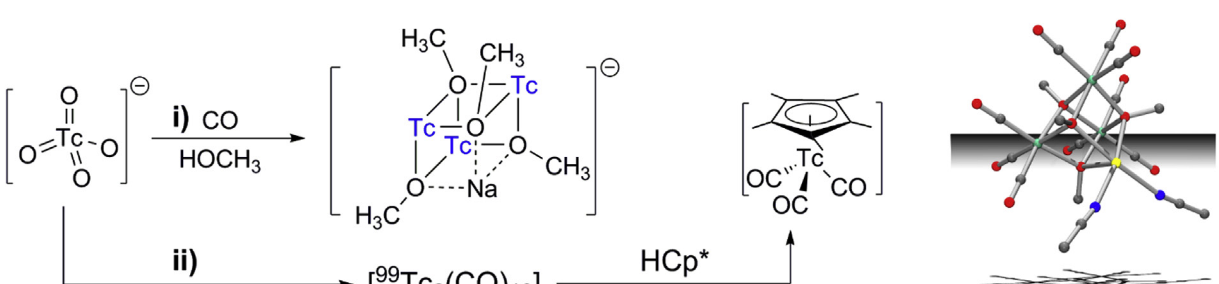
3. From high- to low-valent ^{99}Tc complexes; Carbonyls

The comparably easy synthesis of [Cp*ReO$_3$] from [Cp*Re(CO)$_3$] by oxidation with air, H$_2$O$_2$ or Mn$_2$O$_7$ could not immediately be repeated since the precursor [^{99}Tc$_2$(CO)$_{10}$], was not available. To prepare it on a larger scale was essentially impossible due to the high pressure high temperature conditions [12]. Impossibilities are incentives and this one ultimately led the author into low-valent ^{99}Tc chemistry, useful for radiopharmaceutical chemistry but also for a basic understanding of organometallic technetium chemistry. But first, in the Sattelberger group at the Los Alamos National Laboratory, ^{99}Tc$_2$(CO)$_{10}$ was prepared on a 10–20 g scale, easily possible at that time at that place. A preceding reaction in a Parr pressure vessel with which the conditions according to Heinekey et al. could not be achieved, produced the first carbonyl cluster of technetium, Na[^{99}Tc$_3$(μ$_3$-OCH$_3$)(μ-OCH$_3$)$_3$(CO)$_9$] [13], (Scheme 2), more or less by chance. Whereas rhenium generally precedes research in analogous technetium chemistry, here it was the other way round since this cluster initiated research on similar rhenium mixed-metal system [14,15].

The preparation of [Cp*^{99}Tc(CO)$_3$] caused no problem at all and followed classical organometallic procedures [16]. The compound itself resisted all attempts to be oxidized to [Cp*^{99}TcO$_3$] until to date. Mn$_2$O$_7$ self-decomposed, oxone gave essentially [^{99}TcO$_4$]$^-$ and other powerful oxidants were unsuccessful as well. The reaction with H$_2$O$_2$ had no productive effect what so ever. Cp*^{99}Tc(CO)$_3$ dissolved in benzene and layered with aqueous 30% H$_2$O$_2$ caused migration of all the radioactivity to the aqueous layer, likely as [^{99}TcO$_4$]$^-$; we thus went from [^{99}TcO$_4$]$^-$ to [^{99}Tc$_2$(CO)$_{10}$] to [Cp*^{99}Tc(CO)$_3$] and then back to (sadly) [^{99}TcO$_4$]$^-$. Theoretical calculations indicated already at that time that [Cp*^{99}TcO$_3$] should exist [17]. It seems that the reaction path is the challenge rather than the compound itself. Still, the principal existence of [Cp*^{99}TcO$_3$] has also been put in question based on a probably misinterpreted X-ray structure analysis [18], an ongoing controversy to be solved in the near future. These examples from high oxidations states of group 7 elements underline once more that technetium is not rhenium and one cannot conclude from the behaviour of one element to the other. Around about the same time, Bryan and coworkers published a paper about high-valent organometallic ^{99}Tc complexes that is worth mentioning in this overview. Wilkinson and Herrmann had previously studied complexes with the [Re(=NR)$_3$]$^+$ core, isoelectronic to the [ReO$_3$]$^+$ (or [^{99}TcO$_3$]$^+$) but much less reactive [19,20]. In extension to their rhenium chemistry, Bryan described and fully characterized the ^{99}Tc^{VII} complex [(η^1-C$_5$H$_5$)^{99}Tc(NAr)$_3$] (Ar = 2,6-diisopropyl-phenyl). This air - and water stable ^{99}Tc^{VII} complex can be considered as an electronic analogue of the corresponding tri-oxo complexes. It was hypothesized that the η^1-coordination is due to the much stronger donor abilities of the imido - over the oxo ligands [21,22].

4. Exploring the carbonyls; organometallic chemistry in water

Since there was no ^{99}Tc$_2$(CO)$_{10}$ left or available somewhen at that time, the need for a low pressure synthesis arose. Although very fundamental in the beginning, this question for ambient CO pressure synthesis of ^{99}Tc carbonyl complexes produced ultimately a new synthon for radiopharmaceutical chemistry; the *fac*-



Scheme 2. From [^{99}TcO$_4$]$^-$ to [Cp*^{99}Tc(CO)$_3$]; i) under 90 atm CO pressure in a Parr pressure vessel at 150 °C ii) at 220 atm CO initial pressure and conditions as reported for rhenium by Heinekey et al. [12], Tc denominates the [^{99}Tc(CO)$_3$]$^+$ core (left). X-ray structure of the cluster Na[^{99}Tc$_3$(μ$_3$-OCH$_3$)(μ-OCH$_3$)$_3$(CO)$_9$]·2CH$_3$CN [13].

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