$\{\text{Tc}(\text{NO})(\text{Cp})(\text{PPh}_3)\}^+$ – a novel technetium(I) core†

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Reactions between $[\text{Tc}^{\text{I}}(\text{NO})\text{X}_2(\text{PPh}_3)_2(\text{CH}_3\text{CN})]$ complexes ($\text{X} = \text{Cl}, \text{Br}$) and KCp form the pseudotetrahedral organotechnetium compounds $[\text{Tc}^{\text{I}}(\text{NO})(\text{Cp})(\text{PPh}_3)\text{X}]$. The halide ligands can readily be replaced by other halides or organometallic ligands giving access to a novel family of technetium(I) compounds with the robust $\{\text{Tc}(\text{NO})(\text{Cp})(\text{PPh}_3)\}^+$ core.

There is considerable interest in organotechnetium compounds as potential building blocks in bioconjugates for nuclear medical imaging.^{1–7} Many such approaches use the tricarbonyl core $\{\text{Tc}(\text{CO})_3\}^+$, which can readily be accessed using the IsoLink kit and is used for the complexation of a large variety of preferably tripodal ligand systems.^{7–10} Also promising attempts with cyclopentadienyl (Cp^-) derivatives have been described recently.^{11–15} Nevertheless, there is an enormous lack of structural information about organotechnetium compounds, since the corresponding rhenium complexes are frequently only insufficient models, particularly for non-tricarbonyl compounds and when redox processes are involved in the synthetic procedures.

Complexes of technetium with Cp^- derivatives are rare and only 14 of them have hitherto been characterized unambiguously by X-ray crystallography,^{16–26} while more than 800 entries for the corresponding rhenium compounds can be found in the CSD database.²⁷ This lack of knowledge has not only to do with the radioactivity of technetium, but also with the fact that the ^{99}Tc analogues of many precursors used for the synthesis of organorhenium compounds are difficult to access, less stable and/or volatile. At first glance, it is particularly surprising that the chemistry of nitrosyltechnetium complexes with cyclopentadienyl ligands has not yet been considered so far, since there exist a vast number of papers, which describe the fascinating chemistry of compounds of the general composition $[\text{Re}(\text{NO})(\text{Cp})(\text{PPh}_3)\text{X}]^{0+}$, where X can be almost any monodentate

ligand or organometallic building block.^{28–34} A closer look at this point, however, shows that the synthetic approach to the $\{\text{Re}(\text{NO})(\text{Cp})(\text{PPh}_3)\}^+$ core, particularly to the excellent precursor molecule $[\text{Re}(\text{NO})(\text{Cp})(\text{PPh}_3)\text{Cl}]$, cannot readily be adopted for the chemistry of technetium. It commonly starts from carbonyl species with subsequent reduction of a CO ligand to formyl and methyl and the final replacement of the methyl unit by Cl^- . Such a procedure is still a challenge to be done with ^{99}Tc , even when an improved synthesis for $(\text{NEt}_4)_2[^{99}\text{TcCl}_3(\text{CO})_3]$ has been reported recently.³⁵

In the present communication we describe a convenient synthesis of $[\text{Tc}(\text{NO})(\text{Cp})(\text{PPh}_3)\text{Cl}]$ (1) and some ongoing reactions (Fig. 1), which qualify this compound as a suitable precursor for the further exploration of the chemistry of the $\{\text{Tc}(\text{NO})(\text{Cp})(\text{PPh}_3)\}^+$ core.

$[\text{Tc}(\text{NO})\text{X}_2(\text{PPh}_3)_2(\text{CH}_3\text{CN})]$ ($\text{X} = \text{Cl}, \text{Br}$) complexes react with an excess of KCp in refluxing toluene during the formation of red solids of the compositions $[\text{Tc}(\text{NO})(\text{Cp})(\text{PPh}_3)\text{X}]$ ($\text{X} = \text{Cl}$: 1, $\text{X} = \text{Br}$: 2). Crystalline products could be obtained after filtration over silica gel and recrystallization from CH_2Cl_2 /hexane. The compounds are stable in air. Their infrared spectra show the $\nu(\text{NO})$ bands around 1680 cm^{-1} , which is the typical range of technetium(I) compounds.^{36,37} The ^1H -NMR spectra show singlets of the η^5 -bonded cyclopentadienyl rings integrating to 5 protons at 5.12 ppm (1) and 5.11 ppm (2). The ^{31}P resonances of the respective compounds appear at 29.5 and 29.7 ppm.

The molecular structure of 2 (Fig. 2) reveals the expected pseudotetrahedral structure with a η^5 -bonded cyclopentadienyl ring. It is similar to that of the analogous rhenium complex $[\text{Re}(\text{NO})(\text{MeCp})(\text{PPh}_3)\text{I}]$.³⁸ Crystal structure data of the corresponding $[\text{Re}(\text{NO})(\text{Cp})(\text{PPh}_3)\text{X}]$ complexes ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) are unfortunately not available. The measured bond lengths and

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Fig. 1 Synthesis and reactions of $[\text{Tc}(\text{NO})(\text{Cp})(\text{PPh}_3)\text{X}]$ ($\text{X} = \text{Cl}, \text{Br}$) complexes.

Fig. 2 Structure of **2**. Selected bond lengths: Tc–N 1.869(9), N–O1 1.03(1), Tc–P 2.369(8), Tc–Br 2.471(9), and Tc–Cp(centroid) 1.937(2) Å.

Fig. 3 Structure of the cation of **3**. Selected bond lengths: Tc–N 1.679(8), N–O1 1.155(3), Tc–P 2.369(8), Tc–C(carbonyl) 1.832(2), C–O2 1.133(3), and Tc–Cp(centroid) 1.944(1) Å.

angles are unexceptional and confirm the results derived from the spectroscopic data. The nitrosyl ligand is almost linearly coordinated and acts as a 3-electron donor as has been observed in all hitherto studied $\text{Tc}(\text{NO})$ complexes.^{36,37,39–46}

Compound **1** has been used for some fundamental reactions in order to review its suitability as a precursor for the synthesis of more organotechnetium compounds and to find out restricting conditions for such ongoing reactions. A summary of the first results is given in Fig. 1. It becomes evident that the Cl^- ligand can readily be replaced under conservation of the $\{\text{Tc}(\text{NO})(\text{Cp})(\text{PPh}_3)\}^+$ core. Reactions with HBr or Me_3SiBr give the bromide derivative, which can also be prepared directly from $[\text{Tc}^{\text{IV}}(\text{NO})\text{Br}_2(\text{PPh}_3)_2(\text{CH}_3\text{CN})]$.

Bubbling CO gas through a solution of **1** and addition of $\text{Ag}(\text{BF}_4)$ results in the formation of red crystals of $[\text{Tc}(\text{NO})(\text{Cp})(\text{PPh}_3)(\text{CO})](\text{BF}_4)$ (**3**). The compound is soluble in common organic solvents and stable in air. Its IR spectrum shows the $\nu_{(\text{CO})}$ band at 2037 cm^{-1} , while the $\nu_{(\text{NO})}$ frequency appears at 1776 cm^{-1} . The latter, relatively high value reflects a lower degree of backdonation to the nitrosyl ligand in **3** compared to **1** or **2**. A similar trend of the $\nu_{(\text{NO})}$ bands is also observed for the analogous rhenium compounds. A comparison is given in the ESI† (Table S9).

An ellipsoid plot of the structure of the complex cation of **3** is shown in Fig. 3. Bond lengths and angles of the remaining

coordination sphere are not significantly influenced by the replacement of Cl^- by CO .

The reaction of **1** with phenyl magnesium bromide gives the phenyl derivative **4** in good yields. The synthetic procedure was adopted from that of the analogous Re compound.⁴⁷ Also the solid state structure of **4** corresponds to that of $[\text{Re}(\text{NO})(\text{Cp})(\text{PPh}_3)(\text{Ph})]$, which means that both compounds crystallize in the polar space group $P2_1$ with only one enantiomer of the chiral complex in the crystals, while **2** and **3** crystallize in centrosymmetric space groups as racemates. An ellipsoid plot of **4** is shown in Fig. 4. The Tc–phenyl bond length in **4** of $2.149(2)\text{ Å}$ is in the magnitude of the few other hitherto studied Tc–aryl bonds.⁴⁸ It is interesting to note that the orientation of the phenyl ligand is almost identical to that in the analogous rhenium complex with angles of $69.28(7)^\circ$ and $-16.51(5)^\circ$ between the least-squares plane of the phenyl ring and the Tc–P and Tc–N bonds. In such rotamers, the hydrogen atoms attached to C1 and C42 come close together (2.89 Å in the rhenium complex and $2.398(1)\text{ Å}$ in **4**), see Fig. S3 (ESI†). In solution, there is no evidence for such interactions as is reflected by the NMR spectra of the compounds. That of **4** shows one sharp singlet for the cyclopentadienyl protons at 5.10 ppm and an unexceptional coupling pattern for

Fig. 4 Structure of **4**. Selected bond lengths: Tc–N 1.758(2), N–O 1.198(2), Tc–P 2.357(1), Tc–C 2.47(1), Tc–C(phenyl) 2.149(2), and Tc–Cp(centroid) 1.972(1) Å.

the phenyl ligand, the signals of which are well separated from those of PPh_3 .

^{99}Tc -NMR spectroscopy is a helpful tool for the characterization particularly of $\text{Tc}(\text{VII})$ and $\text{Tc}(\text{I})$ compounds. The nucleus has a high NMR sensitivity, which is relative to the ^1H resonance, 0.275,⁴⁹ but the signals frequently show large line-widths due to the noticeable quadrupole moment of $Q = -0.19(5) \times 10^{-28} \text{ m}^2$.⁵⁰ This is also the case for the pseudotetrahedral compounds of the present study, which all have four different ligands each and show ^{99}Tc -NMR signals with line-widths between 3900 and 8800 Hz. Nevertheless, the spectra can readily be recorded within a reasonable time. The signals appear between -231 and -1753 ppm (Fig. 5), which is typical for $\text{Tc}(\text{I})$ compounds.⁵¹ Such a large range of chemical shifts for structurally closely related compounds indicates a significant influence of the Cl^- , Br^- , Ph^- and CO ligands on the electronic situation of the technetium atoms. For a more quantitative discussion of this point, however, more representatives are required.

There is an ongoing discussion about the existence of the $\text{Tc}(\text{VII})$ compound $[\text{TcO}_3(\text{Cp})]$.^{52–54} All attempts to isolate a molecular compound analogous to $[\text{ReO}_3(\text{Cp})]$, e.g. by the oxidation of $[\text{Tc}(\text{CO})_3(\text{Cp})]$ with H_2O_2 or other oxidants, were hitherto without success,^{19,54,55} and there is some discussion about the general non-existence of this technetium compound.⁵⁴ This stimulated us to attempt oxidation reactions starting from the novel Cp compounds. Reactions of **1** or **2** with H_2O_2 in acetonitrile directly give pertechnetate. The starting materials as well as the product are well detected by ^{99}Tc -NMR spectroscopy, and we could not

Fig. 5 ^{99}Tc -NMR spectra of the pseudotetrahedral $\text{Tc}(\text{I})$ complexes at 20°C .

Fig. 6 Frozen solution X-band EPR spectra of **5** in CH_2Cl_2 at 77 K ($g_{\parallel} = 2.042(1)$, $A_{\parallel}^{\text{Tc}} = 237.3 (\pm 1.0) \times 10^{-4} \text{ cm}^{-1}$, $g_{\perp} = 2.059(1)$, $A_{\perp}^{\text{Tc}} = 104.21 (\pm 1.0) \times 10^{-4} \text{ cm}^{-1}$).

find any evidence for the formation of $[\text{TcO}_3(\text{Cp})]$ or other Tc^{I} or Tc^{VII} intermediates during the corresponding NMR experiment.

The lability of the Cp^- ligand in the title complexes upon oxidation is also shown during another experiment: the oxidation of **2** with equivalent amounts of bromine, which gives the technetium(II) complex $[\text{Tc}(\text{NO})\text{Br}_3(\text{OPPh}_3)_2]$ (**5**) as the exclusive product, while similar reactions with $[\text{Re}(\text{Cp})(\text{CO})_3]$ or $[\text{Tc}(\text{Cp}^*)(\text{CO})_3]$ gave $[\text{M}^{\text{III}}(\text{Cp}^*)\text{Br}_2(\text{CO})_2]$ ($\text{M} = \text{Tc}, \text{Re}$) and $[\text{Tc}^{\text{III}}(\text{Cp}^*)\text{Br}(\text{CO})_3]^+$, respectively.^{19,55} Compound **5** (for an ellipsoid plot see Fig. S4 of the ESI[†]) is a hitherto unknown member of the family of octahedral phosphine/phosphine oxide nitrosyltechnetium(II) complexes, with one of the OPPh_3 ligands being coordinated equatorially, while the second one is in the *trans* position to NO. The Tc–O bond to the latter one is slightly lengthened indicating a considerable *trans* influence of the nitrosyl ligand. While the room temperature EPR spectrum of the $\text{Tc}(\text{II})$ compounds shows the expected 10-line hyperfine structures (hfs) due to the interaction of the unpaired electron with the nuclear spin of ^{99}Tc ($I = 9/2$), the anisotropic EPR spectrum of a frozen solution of the compound (Fig. 6) has axially-symmetric features with resolved ^{99}Tc hfs patterns in the parallel and perpendicular parts.

In conclusion, previously unreported technetium Cp complexes have been synthesized, closing a gap in the organometallic chemistry of the homologous elements technetium and rhenium. The ready synthesis of the parent complexes **1** and **2** recommends them as precursors for ongoing work in order to explore the full synthetic potential of the $\{\text{Tc}(\text{NO})(\text{Cp})(\text{PPh}_3)_2\}^+$ core. Such experiments will be the subject of further studies in our laboratory, also including attempts to find an approach to related $^{99\text{m}}\text{Tc}$ compounds for nuclear medical procedures.

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