



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

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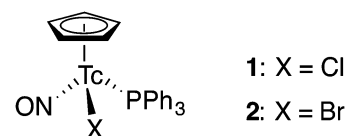
Reactions between $[\text{Tc}^{\text{I}}(\text{NO})\text{X}_2(\text{PPh}_3)_2(\text{CH}_3\text{CN})]$ complexes (X = Cl, Br) and KCp form the pseudotetrahedral organotechnetium compounds $[\text{Tc}^{\text{I}}(\text{NO})(\text{Cp})(\text{PPh}_3)\text{X}]$. The halide ligands can readily be replaced by 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 ⁹⁹Tc 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 ⁹⁹Tc, even when an improved synthesis for $(\text{NEt}_4)_2[\text{TcCl}_3(\text{CO})_3]$ 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.



$[\text{Tc}(\text{NO})\text{X}_2(\text{PPh}_3)_2(\text{CH}_3\text{CN})]$ (X = Cl, Br) complexes react with an excess of KCp in refluxing toluene during the formation of red solids of the compositions $[\text{Tc}(\text{NO})(\text{Cp})(\text{PPh}_3)\text{X}]$ (X = Cl: **1**, X = Br: **2**). Crystalline products could be obtained after filtration over silica gel and recrystallization from CH₂Cl₂/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 ³¹P 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 (X = Cl, Br, I) are unfortunately not available. The measured bond lengths and

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† Electronic supplementary information (ESI) available: Synthetic procedures, spectroscopic data and details about the structural determinations, and tables with bond lengths and angles. CCDC 1491441–1491444. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c6cc05811f



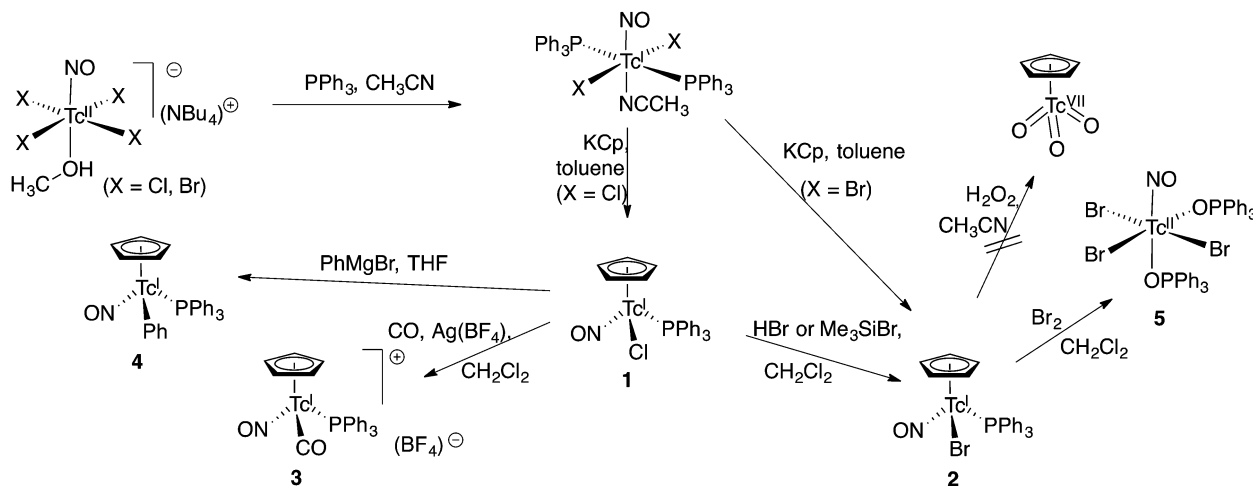


Fig. 1 Synthesis and reactions of $[\text{Tc}(\text{NO})(\text{Cp})(\text{PPh}_3)\text{X}]$ ($\text{X} = \text{Cl}, \text{Br}$) complexes.

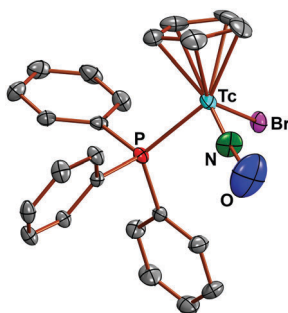


Fig. 2 Structure of **2**. Selected bond lengths: Tc–N 1.869(9), N–O 1.03(1), Tc–P 2.369(8), Tc–Br 2.471(9), and Tc–Cp(centroid) 1.937(2) Å.

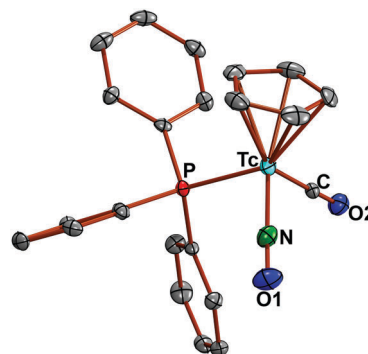


Fig. 3 Structure of the cation of **3**. Selected bond lengths: Tc–N 1.679(8), N–O 1.155(3), Tc–P 2.369(8), Tc–C(carbonyl) 1.832(2), C–O 1.133(3), and Tc–Cp(centroid) 1.944(1) Å.

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 Tc(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 $[\text{Tc}(\text{NO})\text{Br}_2(\text{PPh}_3)_2(\text{CH}_3\text{CN})]$.

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



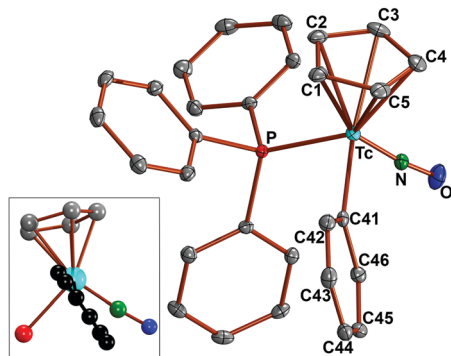


Fig. 4 Structure of **4**. Selected bond lengths: Tc–N 1.758(2), N–O 1.198(2), Tc–P 2.357(1), Tc–C 2.47(1), Tc–C(phenyl) 2.149(2), and Tc–Cp(centroid) 1.972(1) Å.

the phenyl ligand, the signals of which are well separated from those of PPh₃.

⁹⁹Tc-NMR spectroscopy is a helpful tool for the characterization particularly of Tc(VII) and Tc(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 ⁹⁹Tc-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 Tc(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 Tc(VII) compound [TcO₃(Cp)].^{52–54} All attempts to isolate a molecular compound analogous to [ReO₃(Cp)], *e.g.* by the oxidation of [Tc(CO)₃(Cp)] with H₂O₂ 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 H₂O₂ in acetonitrile directly give pertechnetate. The starting materials as well as the product are well detected by ⁹⁹Tc-NMR spectroscopy, and we could not

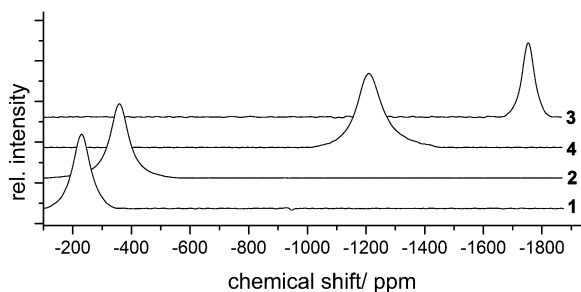


Fig. 5 ⁹⁹Tc-NMR spectra of the pseudotetrahedral Tc(I) complexes at 20 °C.

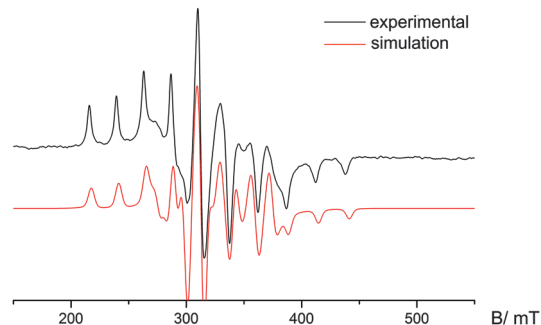


Fig. 6 Frozen solution X-band EPR spectra of **5** in CH₂Cl₂ at 77 K ($g_{\parallel} = 2.042(1)$, $A_{\parallel}^{\text{Tc}} = 237.3 (\pm 1.0) \times 10^{-4} \text{ cm}^{-1}$, $g_{\perp} = 2.059(1)$, $A_{\perp}^{\text{Tc}} = 104.21 (\pm 1.0) \times 10^{-4} \text{ cm}^{-1}$).

find any evidence for the formation of [TcO₃(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 [Tc(NO)Br₃(OPPh₃)₂] (**5**) as the exclusive product, while similar reactions with [Re(Cp)(CO)₃] or [Tc(Cp*)(CO)₃] gave [M^{III}(Cp*)Br₂(CO)₂] (M = Tc, Re) and [Tc^{III}(Cp*)Br(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 OPPh₃ 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 Tc(II) compounds shows the expected 10-line hyperfine structures (hfs) due to the interaction of the unpaired electron with the nuclear spin of ⁹⁹Tc ($I = 9/2$), the anisotropic EPR spectrum of a frozen solution of the compound (Fig. 6) has axially-symmetric features with resolved ⁹⁹Tc 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 {Tc(NO)(Cp)(PPh₃)₂}⁺ core. Such experiments will be the subject of further studies in our laboratory, also including attempts to find an approach to related ^{99m}Tc compounds for nuclear medical procedures.

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