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{Tc(NO)(Cp)(PPh₃)}⁺ – a novel technetium(I) core†

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Reactions between [Tcᴵ(NO)X₂(PPh₃)₂(CH₃CN)] complexes (X = Cl, Br) and KCp form the pseudotetrahedral organotechnetium compounds [Tcᴵ(NO)(Cp)(PPh₃)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 {Tc(NO)(Cp)(PPh₃)}⁺ 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 {⁹⁹ᵐTc(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 [Re(NO)(Cp)(PPh₃)X]⁰,⁺, where X can be almost any monodentate

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ligand or organometallic building block.[28–34] A closer look at this point, however, shows that the synthetic approach to the {Re(NO)(Cp)(PPh₃)}⁺ core, particularly to the excellent precursor molecule [Re(NO)(Cp)(PPh₃)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 (NEt₄)₂[⁹⁹TcCl₃(CO)₃] has been reported recently.[35]

In the present communication we describe a convenient synthesis of [Tc(NO)(Cp)(PPh₃)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 {Tc(NO)(Cp)(PPh₃)}⁺ core.

1: X = Cl
2: X = Br
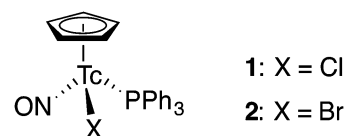
[Tc(NO)X₂(PPh₃)₂(CH₃CN)] (X = Cl, Br) complexes react with an excess of KCp in refluxing toluene during the formation of red solids of the compositions [Tc(NO)(Cp)(PPh₃)X] (X = Cl: **1**, X = Br: **2**). Crystalline products could be obtained after filtration over silica gel and recrystallization from CH₂Cl₂/hexane. The compounds are stable in air. Their infrared spectra show the $\nu_{(NO)}$ bands around 1680 cm⁻¹, which is the typical range of technetium(I) compounds.[36,37] The ¹H-NMR spectra show singlets of the η⁵-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 η⁵-bonded cyclopentadienyl ring. It is similar to that of the analogous rhenium complex [Re(NO)(MeCp)(PPh₃)I].[38] Crystal structure data of the corresponding [Re(NO)(Cp)(PPh₃)X] complexes (X = Cl, Br, I) are unfortunately not available. The measured bond lengths and

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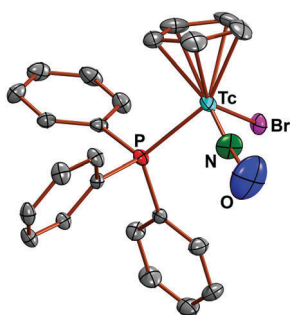

Fig. 2 Structure of **2**. Selected bond lengths: Tc−N 1.869(9), N−O1 1.03(1), Tc−P 2.369(8), Tc−Br 2.471(9), and Tc−Cp(centroid) 1.937(2) Å.
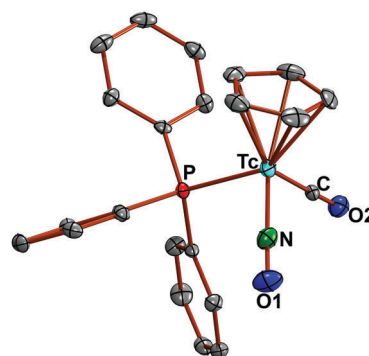

Fig. 3 Structure of the cation of **3**. Selected bond lengths: Tc−N 1.679(8), N−O1 1.155(3), Tc−P 2.369(8), Tc−C(carbonyl) 1.832(2), C−O2 1.133(3), and Tc−Cp(centroid) 1.944(1) Å.

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 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 {Tc(NO)(Cp)(PPh$_3$)}$^+$ core. Reactions with HBr or Me$_3$SiBr give the bromide derivative, which can also be prepared directly from [Tc^I(NO)Br$_2$(PPh$_3$)$_2$(CH$_3$CN)].

Bubbling CO gas through a solution of **1** and addition of Ag(BF$_4$) results in the formation of red crystals of [Tc(NO)(Cp)-(PPh$_3$)(CO)][BF$_4$] (**3**). The compound is soluble in common organic solvents and stable in air. Its IR spectrum shows the $\nu_{(CO)}$ band at 2037 cm^{-1}, while the $\nu_{(NO)}$ 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 $\nu_{(NO)}$ 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 [Re(NO)(Cp)(PPh$_3$)(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) 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)° and −16.51(5)° 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) 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
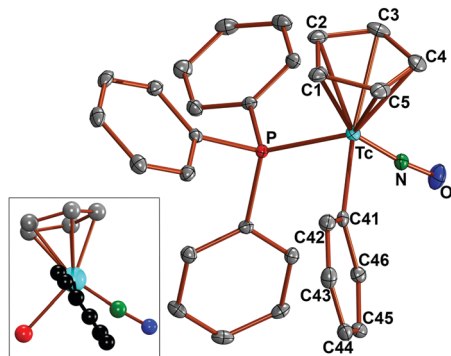
Fig. 4 Structure of **4**. Selected bond lengths: Tc–N 1.758(2), N–O 1.198(2), Tc–P 2.357(1), Tc–C 2.47(1), Tc–C(phenyl) 2.149(2), and Tc–Cp(centroid) 1.972(1) Å.

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

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

^{99}Tc-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 ^{1}H resonance, 0.275,[49] but the signals frequently show large line-widths due to the noticeable quadrupole moment of $Q = -0.19(5) \times 10^{-28}$ m².[50] This is also the case for the pseudotetrahedral compounds of the present study, which all have four 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 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 ^{99}Tc-NMR spectroscopy, and we could not
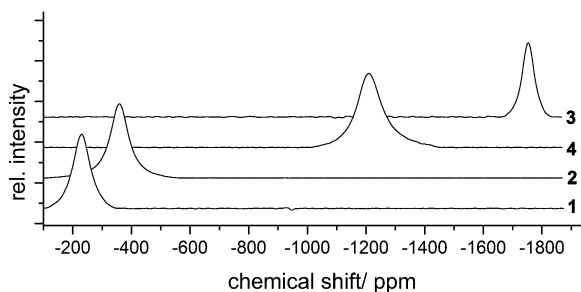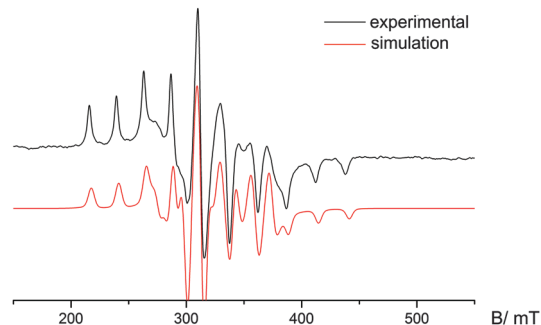
find any evidence for the formation of [TcO₃(Cp)] or other Tc^I or Tc^{VII} intermediates during the corresponding NMR experiment.

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 ^{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 {Tc(NO)(Cp)(PPh₃)}⁺ 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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Fig. 5 ^{99}Tc-NMR spectra of the pseudotetrahedral Tc(I) complexes at 20 °C.

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