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# $[\{\text{Tc}^{\text{I}}(\text{NO})(\text{L}^{\text{OMe}})(\text{PPh}_3)\text{Cl}\}_2\text{Ag}](\text{PF}_6)$ and $[\text{Tc}^{\text{II}}(\text{NO})(\text{L}^{\text{OMe}})(\text{PPh}_3)\text{Cl}](\text{PF}_6)$ : Two Unusual Technetium Complexes with a “Kläui-type” Ligand

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The reaction of  $[\text{Tc}^{\text{I}}(\text{NO})(\text{L}^{\text{OMe}})(\text{PPh}_3)\text{Cl}]$  ( $\{\text{L}^{\text{OMe}}\}^- = \eta^5\text{-cyclopentadienyltris(dimethyl phosphito-}P\text{)cobaltate(III)}$ ) with  $\text{Ag}(\text{PF}_6)$  gives two unexpected products: the dimeric technetium(I) complex  $[\{\text{Tc}(\text{NO})(\text{L}^{\text{OMe}})(\text{PPh}_3)\text{Cl}\}_2\text{Ag}](\text{PF}_6)$  with a

central  $\text{Ag}^+$  ion and the cationic Tc(II) compound  $[\text{Tc}(\text{NO})(\text{L}^{\text{OMe}})(\text{PPh}_3)\text{Cl}](\text{PF}_6)$ . The products have been studied spectroscopically and by X-ray diffraction.

## Introduction

Technetium complexes are of ongoing interest as potential radiopharmaceuticals. The metastable nuclear isomer  $^{99\text{m}}\text{Tc}$  is by far the most frequently used nuclide in diagnostic nuclear medicine with some 40 million administrations annually.<sup>[1]</sup> Since the introduction of a technetium(I) isocyanide complex into the routine myocardial imaging in the 1980's,<sup>[2–6]</sup> also organometallic approaches found an increasing interest. This includes numerous compounds with the  $\{^{99\text{m}}\text{Tc}(\text{CO})_3\}^+$  core,<sup>[7–9]</sup> but also bis-arene complexes, and particularly cyclopentadienyl ( $\text{Cp}^-$ ) compounds.<sup>[8,10–15]</sup>

Recently, we reported a number of technetium complexes having the  $\{\text{Tc}(\text{NO})(\text{Cp})(\text{PPh}_3)\}^+$  core.<sup>[16,17]</sup> The chlorido ligand of their parent compound  $[\text{Tc}(\text{NO})(\text{Cp})(\text{PPh}_3)\text{Cl}]$  (**1**) can readily be replaced by other anionic or neutral ligands. Stimulated by the versatility of this core, we decided to undertake some efforts for the synthesis of similar compounds with ligands, which are isolobal to  $\text{Cp}^-$ . The classical scorpionate tris(pyrazolyl)borate, but also  $\eta^5\text{-cyclopentadienyltris(dialkyl phosphito-}P\text{)cobaltates(III)}$  (“Kläui-type” ligands) are frequently discussed a surrogates for the 6-electron donor  $\text{Cp}^-$ .<sup>[18–21]</sup> A variety of technetium complexes with the “Kläui-type” ligand  $\eta^5\text{-}$

cyclopentadienyltris(dimethyl phosphito-*P*)cobaltate(III) ( $\{\text{L}^{\text{OMe}}\}^-$ ), comprising seven different oxidation states of the transition metal have been introduced recently.<sup>[22]</sup> The obtained products are of remarkable stability, which recommends them as starting materials for ongoing reactions. One of the isolated technetium(I) complexes,  $[\text{Tc}(\text{NO})(\text{L}^{\text{OMe}})(\text{PPh}_3)\text{Cl}]$  (**2**) in Figure 1, is structurally related to the cyclopentadienyl compound **1**, for which we recently had to note some unexpected behavior.<sup>[23]</sup> An illustrative example is the reaction of **1** with  $\text{Ag}(\text{PF}_6)$ . Not all chlorido ligands are abstracted from technetium in this reaction and the dimeric, chlorido-bridged complex  $[\{\text{Tc}(\text{NO})(\text{Cp})(\text{PPh}_3)\}_2\text{Cl}](\text{PF}_6)$  is formed instead.

In the present communication, we report about a similar reaction with the corresponding complex containing a “Kläui-type” ligand (**2**) and the structures of the formed products.

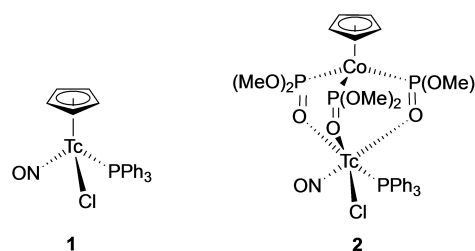
## Results and Discussion

The starting material  $[\text{Tc}(\text{NO})(\text{L}^{\text{OMe}})(\text{PPh}_3)\text{Cl}]$  (**2**) can be prepared from a simple ligand exchange reaction between  $[\text{Tc}(\text{NO})\text{Cl}_2(\text{PPh}_3)_2(\text{CH}_3\text{CN})]$  and  $\text{NaL}^{\text{OMe}}$  in reasonable yields and with high purity.<sup>[22]</sup> No redox processes or the formation of considerable amounts of side-products have been observed during the synthesis. The compound is stable in air, but cyclic voltammetry gave evidence for a quasi-reversible one-electron

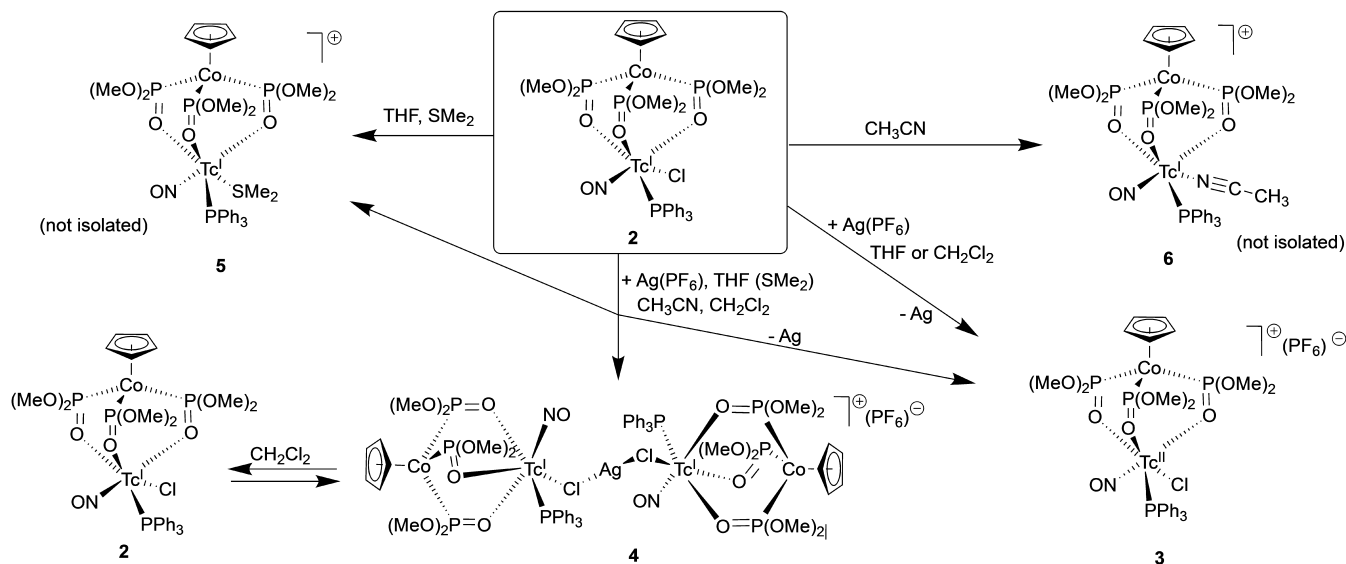
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**Figure 1.** Technetium(I) complexes with (pseudo)tripodal ligands:  $[\text{Tc}(\text{NO})(\text{Cp})(\text{PPh}_3)\text{Cl}]$  (**1**) and  $[\text{Tc}(\text{NO})(\text{L}^{\text{OMe}})(\text{PPh}_3)\text{Cl}]$  (**2**).



Scheme 1. Reactions of  $[\text{Tc}(\text{NO})(\text{L}^{\text{OMe}})(\text{PPh}_3)\text{Cl}]$  (**2**) with  $\text{Ag}(\text{PF}_6)$ .

oxidation with a half-wave potential of  $-0.16$  V vs. ferrocene.<sup>[22]</sup>

An attempted oxidation of **2** with  $\text{Cl}_2$  gave a mixture of various Tc(II) nitrosyl complexes, where one of which could be assigned to the  $[\text{Tc}(\text{NO})\text{Cl}_4(\text{solvent})]^-$  anion on the basis of its EPR data.<sup>[24]</sup>

A more selective formation of a Tc(II) complex is obtained when solutions of **2** in THF or  $\text{CH}_2\text{Cl}_2$  are exposed to  $\text{Ag}(\text{PF}_6)$ . This reaction results in a rapid dissolution of the sparingly soluble starting material and the deposition of a small amount of a grey solid (elemental silver), which can readily be filtered off. Upon concentration of the resulting solution, the red solid technetium(II) complex  $[\text{Tc}(\text{NO})(\text{L}^{\text{OMe}})(\text{PPh}_3)\text{Cl}](\text{PF}_6)$  (**3**) precipitates (Scheme 1). The oxidation state of the product can be derived from the  $\nu_{\text{NO}}$  stretch, which appears as an intense band at  $1786\text{ cm}^{-1}$ , the typical range for Tc(II) complexes. The IR spectra of the more electron-rich technetium(I) complexes show their  $\nu_{\text{NO}}$  absorptions at clearly lower frequencies due to a higher degree of back-donation from orbitals of the  $d^6$  Tc(I) ion into antibonding orbitals of the NO ligand.<sup>[22,24,25]</sup>

The  $d^5$  "low-spin" configuration of Tc(II) allows the detection of resolved EPR spectra. Figure 2 depicts the spectra obtained for compound **3**. At room-temperature, a well resolved 10-line pattern is observed, which is expected from the interaction of the unpaired electron with the nuclear spin of  $^{99}\text{Tc}$  ( $I=9/2$ ). A frozen solution of the compound shows a more complex, axially symmetric EPR spectrum with two sets of 10-line patterns for the parallel and perpendicular parts as can be described by the following spin Hamiltonian:

$$\hat{H}_{sp} = \beta_e \left[ g_{\parallel} H_z \hat{S}_z + g_{\perp} (H_x \hat{S}_x + H_y \hat{S}_y) \right] + A_{\parallel}^{\text{Tc}} \hat{I}_z \hat{S}_z + A_{\perp}^{\text{Tc}} (\hat{I}_x \hat{S}_x + \hat{I}_y \hat{S}_y) + A_{\perp}^{\text{Tc}} (\hat{I}_x \hat{S}_x + \hat{I}_y \hat{S}_y) + Q' \left[ \hat{I}_z^2 - 1/3 I(I+1) \right],$$

where  $g_{\parallel}$ ,  $g_{\perp}$ ,  $A_{\parallel}^{\text{Tc}}$  and  $A_{\perp}^{\text{Tc}}$  are the principle values of the  $\tilde{g}$  and the  $^{99}\text{Tc}$  hyperfine interaction tensors. The  $^{99}\text{Tc}$  quadrupole coupling constant  $Q'$  is small and was neglected.

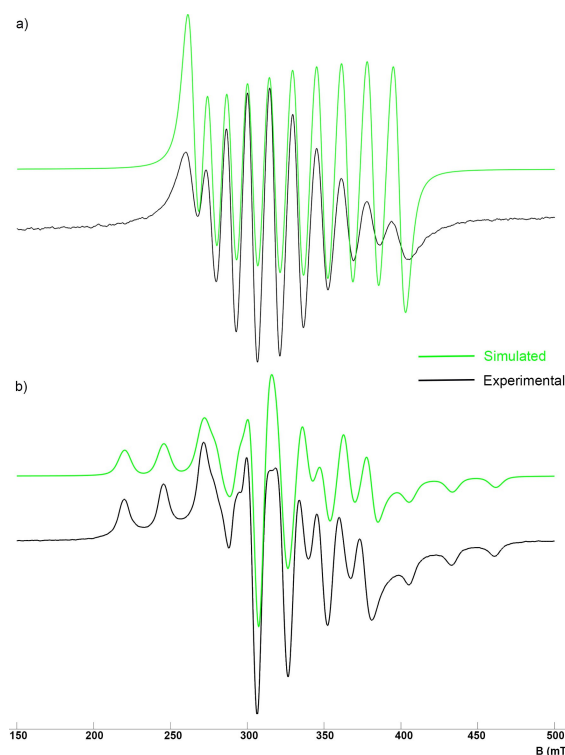
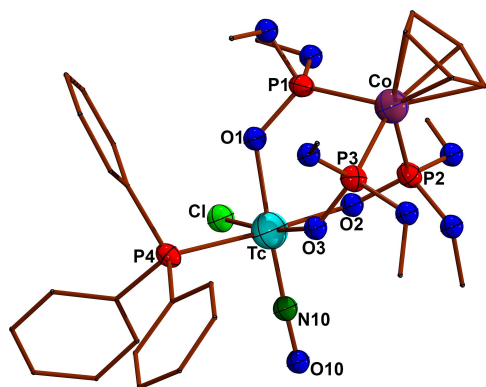


Figure 2. X-Band EPR spectra of  $[\text{Tc}(\text{NO})(\text{L}^{\text{OMe}})(\text{PPh}_3)\text{Cl}](\text{PF}_6)$  in  $\text{CH}_2\text{Cl}_2$  recorded a) in liquid solution at room temperature and b) in frozen solution at 78 K. EPR parameters:  $g_0 = 2.0247$ ,  $a_0^{\text{Tc}} = 139.5 \cdot 10^{-4}\text{ cm}^{-1}$ ;  $g_{\parallel} = 1.972$ ,  $g_{\perp} = 2.015$ ,  $A_{\parallel}^{\text{Tc}} = 247 \cdot 10^{-4}\text{ cm}^{-1}$ ,  $A_{\perp}^{\text{Tc}} = 100 \cdot 10^{-4}\text{ cm}^{-1}$ ,  $A_{\parallel}^{\text{P}} = 25 \cdot 10^{-4}\text{ cm}^{-1}$ ,  $A_{\perp}^{\text{P}} = 20 \cdot 10^{-4}\text{ cm}^{-1}$ .

The perpendicular part of the spectrum is not fully resolved due to large line widths. They result from superhyperfine interactions of the unpaired electron with the  $^{31}\text{P}$  nucleus of  $\text{PPh}_3$ . Although these interactions are not resolved in the

experimental spectrum, they can be estimated from line-width considerations to have values of approximately  $25 \cdot 10^{-4} \text{ cm}^{-1}$  for the parallel part and  $20 \cdot 10^{-4} \text{ cm}^{-1}$  for the perpendicular part. The obtained values are in the same magnitude as observed for other nitrosyl or thionitrosyl complexes of technetium(II) as  $[\text{Tc}(\text{NX})\text{Y}_3(\text{PMe}_2\text{PhP})_2]$  ( $\text{X}=\text{O}, \text{S}; \text{Y}=\text{Cl}, \text{Br}$ ) complexes or  $[\text{Tc}(\text{NO})\text{Cl}_3\{(\text{2-aminomethylphenyl})\text{diphenylphosphine}\}]$ .<sup>[26–28]</sup> Unlike the spectra with monodentate phosphines, which have almost isotropic  $\tilde{g}$  tensors,<sup>[25,26]</sup> the spectrum of **3** shows a considerable anisotropy. This is most probably a consequence of the chelate formation and has been observed before for Tc(II) complexes with *P,N*-chelating ligands.<sup>[27]</sup> Interactions with the nitrosyl ligand have not been observed.

The preservation of the coordination sphere of technetium upon oxidation is proven by an X-ray structure determination. Figure 3 shows the structure of the  $[\text{Tc}^{\text{I}}(\text{NO})(\text{L}^{\text{OMe}})(\text{PPh}_3)\text{Cl}]^+$  cation. Selected bond lengths and angles are summarized in Table 1. It is evident that bond lengths and angles around the technetium atoms are not significantly influenced by the oxidation state of the metal. The same holds true for the nitrosyl ligand, which is linearly bound in compounds **2** and compound **3**, and thus, shall be regarded as  $\text{NO}^+$ . This is not surprising and in accord with all other structurally characterized nitrosyl complexes of technetium.<sup>[25]</sup>



**Figure 3.** Structure of  $[\text{Tc}^{\text{I}}(\text{NO})(\text{L}^{\text{OMe}})(\text{PPh}_3)\text{Cl}]^+$ . Hydrogen atoms are omitted for clarity.

**Table 1.** Selected bond lengths (Å) and angles (°) in  $[\text{Tc}^{\text{I}}(\text{NO})(\text{L}^{\text{OMe}})(\text{PPh}_3)\text{Cl}]$  (**2**),  $[\text{Tc}^{\text{II}}(\text{NO})(\text{L}^{\text{OMe}})(\text{PPh}_3)\text{Cl}](\text{PF}_6)$  (**3**) and  $[\{\text{Tc}^{\text{I}}(\text{NO})(\text{L}^{\text{OMe}})(\text{PPh}_3)\text{Cl}_2\text{Ag}\}(\text{PF}_6)]$  (**4**).

	<b>2*</b>	<b>3</b>	<b>4**</b>
Tc–N10	1.709(5)	1.734(11)	1.839(8)/1.689(8)
Tc–Cl1	2.361(2)	2.329(5)	2.388(3)/2.424(2)
Tc–O1	2.134(1)	2.051(3)	2.102(3)/2.110(3)
Tc–O2	2.166(1)	2.067(3)	2.162(3)/2.157(3)
Tc–O3	2.124(1)	2.050(3)	2.094(3)/2.076(3)
Tc–P4	2.359(4)	2.481(1)	2.366(1)/2.373(1)
Ag–Cl			2.624(2)/2.490(2)

\*Values have been taken from ref. 22 and the atomic labelling scheme has been adopted from Figure 3; \*\*Values for two independent molecules.

$[\text{Tc}^{\text{I}}(\text{NO})(\text{L}^{\text{OMe}})(\text{PPh}_3)\text{Cl}](\text{PF}_6)$  is the sole product, when the reaction of **2** with  $\text{Ag}(\text{PF}_6)$  is performed in THF, and there is no evidence for the formation of (intermediate) technetium(I) compounds. This behavior is not unexpected keeping in mind that ether-type ligands such as THF form only very weak bonds to technetium. Up to now, there are only two examples of structurally characterized technetium complexes with monodentate ether ligands,<sup>[29,30]</sup> and there is experimental evidence that even minor traces of water readily replace dioxane from the coordination sphere of technetium.<sup>[31]</sup>

A different behavior is observed, when potential ligands such as dimethylsulfide ( $\text{SMe}_2$ ) or acetonitrile are added to the reaction mixture. The addition of a few drops of  $\text{SMe}_2$  to a solution of **2** in a  $\text{CH}_2\text{Cl}_2/\text{THF}/\text{CH}_3\text{CN}$  mixture prevents the complete oxidation of the starting material and three additional  $^{99}\text{Tc}$  NMR signals are observed. A considerable amount of  $[\{\text{Tc}^{\text{I}}(\text{NO})(\text{L}^{\text{OMe}})(\text{PPh}_3)\text{Cl}_2\text{Ag}\}(\text{PF}_6)]$  (**4**) and a minor amount of another technetium(I) complex, which is most probably  $[\text{Tc}^{\text{I}}(\text{NO})(\text{L}^{\text{OMe}})(\text{PPh}_3)(\text{SMe}_2)]^+$  (**5**) precipitate directly from the reaction mixture together with the technetium(II) complex **3**, while a small amount of a third Tc(I) complex,  $[\text{Tc}^{\text{I}}(\text{NO})(\text{L}^{\text{OMe}})(\text{PPh}_3)(\text{NCCH}_3)]^+$  (**6**), remains in solution. Compounds **5** and **6** have not been isolated in crystalline form and their compositions have been derived on the basis of their  $^{99}\text{Tc}$  NMR resonances at 1305 ppm ( $\nu_{1/2}=2740 \text{ Hz}$ ) (**5**) and 1595 ppm ( $\nu_{1/2}=1290 \text{ Hz}$ ) (**6**). The same spectroscopic features are observed for solutions of **2** in a  $\text{SMe}_2/\text{THF}$  mixture or in neat acetonitrile.

The precipitated compounds **3** and **4** can be separated on the basis of their different solubilities in toluene. This allows a separation of compound **4** by subsequent extraction operations with this solvent, while compound **3** remains as a solid. The purity of the compounds in the two fractions can easily be checked by their IR spectra, where the nitrosyl bands appear clearly separated (**3**:  $1786 \text{ cm}^{-1}$ , **4**:  $1705 \text{ cm}^{-1}$ ). Alternatively, EPR or  $^{99}\text{Tc}$  NMR spectroscopy can be used to prove the purity of the samples.

Single crystals of **4** were obtained directly from the slow evaporation of the reaction mixture.

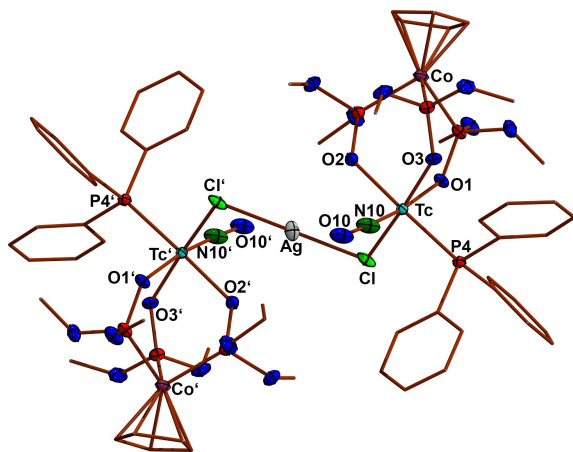
As for all other technetium(I) complexes,<sup>[16,17,22–25]</sup> the  $\nu_{\text{NO}}$  vibration of compound **3** appears as an intense band at a relatively low frequency. This is readily explained by the high degree of back-donation from orbitals of the  $d^6$  Tc(I) ion into  $\pi^*$  orbitals of the NO ligand. The  $^1\text{H}$  NMR spectrum of **4** is unexceptional and shows the expected signals for the aromatic and the methyl protons at almost identical positions as in the parent compound **2**. The same holds true for the  $^{31}\text{P}$  resonances of the chelate-bonded  $\{\text{L}^{\text{OMe}}\}^-$ , which appear as one broad signal at 119.6 ppm. The considerable line broadening of  $^{31}\text{P}$  NMR signals is frequently observed for technetium complexes and result from scalar couplings of  $^{31}\text{P}$  nuclei with the large quadrupole moment of  $^{99}\text{Tc}$ .<sup>[26]</sup> In many cases (as in those of complex **4**, **5** and **6** of the present study, and their parent compound **2**) such broadenings make the  $^{31}\text{P}$  signals of ligands with a Tc–P bond practically invisible.<sup>[22,27]</sup> The large quadrupole moment of  $^{99}\text{Tc}$  ( $Q = -0.19 \cdot 10^{-28} \text{ m}^2$ ) is also responsible for a strong line broadening of the related  $^{99}\text{Tc}$  NMR signals, which is normally observed when  $^{99}\text{Tc}$  complexes with low local

symmetry are studied.<sup>[28]</sup> Nevertheless, this method is a valuable tool for the characterization of preferably Tc(I) and Tc(VII) complexes. Due to the large chemical shift range of <sup>99</sup>Tc NMR from approximately -7000 to +5000 ppm this method is sensitive even to slight changes in the electronic environment and geometry of the <sup>99</sup>Tc nuclei in such compounds.<sup>[29]</sup> The chemical shift of compound **2** appears at 2169 ppm with a line width of approximately 3180 Hz. It is interesting to note that the resonance of the structurally related compound [Tc(NO)(Cp)(PPh<sub>3</sub>)Cl] (**1**) is found in a completely different spectral range (-231 ppm),<sup>[16]</sup> which questions the frequently discussed electronic similarity between Cp<sup>-</sup> and {L<sup>OR</sup>}<sup>-</sup> (R = alkyl) ligands.

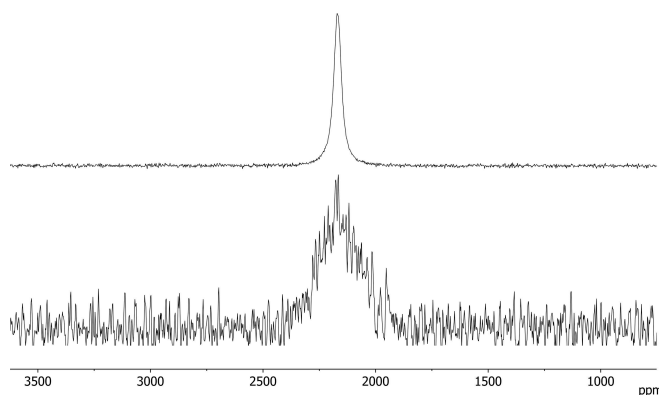
The formation of a cationic complex with a central Ag<sup>+</sup> ion coordinated to the chlorido ligands of two {Tc(NO)(L<sup>OMe</sup>)(PPh<sub>3</sub>)Cl} units is proven by a single crystal X-ray structural analysis. The complex cation is shown in Figure 4 and selected bond lengths and angles are contained in Table 1. The most remarkable feature of the compound is the central {Tc-Cl-Ag-Cl-Tc}<sup>+</sup> unit, which is established between two [Tc(NO)(L<sup>OMe</sup>)(PPh<sub>3</sub>)Cl] complexes in the solid state. The Cl-Ag-Cl bridge is linear, while Tc-Cl-Ag angles of 82.88(7) and 86.37(6)° are established for two crystallographically independent species. Weak silver-oxygen interactions (Ag-O2 distance: 2.628 Å) may support the {Cl-Ag-Cl} bridge.

Compounds with (almost) unsupported AgX<sub>2</sub> bridges (X = halogen) are rare and only a few of them have been studied structurally. Three of them, the polymeric (NBu<sub>4</sub>)<sub>x</sub>[Pt(C<sub>6</sub>C<sub>5</sub>)<sub>2</sub>Cl<sub>2</sub>Ag]<sub>x</sub>, [{Pt(N,N'-Schiff base)Cl(Me)}<sub>2</sub>Ag](BF<sub>4</sub>) and [{Ru<sub>2</sub>(anilinopyridine)<sub>4</sub>AgF<sub>2</sub>](BF<sub>4</sub>)<sub>3</sub> have linear X-Ag-X units,<sup>[32-34]</sup> while the corresponding angles in [{Re(Tp)(N-p-tol)(Ph)}<sub>2</sub>Ag](PF<sub>6</sub>) and [M((C,N,N',P) ligand)(AN)Cl]<sub>2</sub>Ag(SbF<sub>6</sub>)<sub>3</sub> (M = Rh, Ir) are between 120 and 125°.<sup>[35,36]</sup> The Ag-Cl bond in all these compounds are around 2.5 Å as we have found for complex **4** of the present work.

The dimeric solid state structure of the [{Tc<sup>I</sup>(NO)(L<sup>OMe</sup>)(PPh<sub>3</sub>)Cl]<sub>2</sub>Ag}<sup>+</sup> cation is not maintained in solution. As mentioned above, the <sup>1</sup>H and <sup>31</sup>P NMR spectra of **4** in dichloromethane closely resemble those of the starting material **2**, but



**Figure 4.** Structure of the [{Tc<sup>I</sup>(NO)(L<sup>OMe</sup>)(PPh<sub>3</sub>)Cl]<sub>2</sub>Ag}<sup>+</sup> cation. Hydrogen atoms are omitted for clarity.



**Figure 5.** <sup>99</sup>Tc NMR spectra of a) compound **2** and b) compound **4** in CH<sub>2</sub>Cl<sub>2</sub> with a strong line broadening for **4** indicating a dynamic behavior in solution.

they are less intense with respect to the lower solubility of the dimer and show broad lines indicating a dynamic behavior. The <sup>99</sup>Tc NMR signal of **4** appears approximately at the same chemical shift as that of complex **2**, but an extreme line broadening is observed from 3180 Hz for compound **2** to approximately 23.5 kHz for compound **4** (Figure 5). Hence, we propose a dissociation of **4** in solution according to the equilibrium given in Scheme 1. Another strong hint for the existence of such an equilibrium is the gradual formation of the paramagnetic complex **3** in such solutions. This can be evidenced by the detection of its EPR spectrum and understood by the partial oxidation of the Tc(I) complex by the released Ag<sup>+</sup> ions. Such a reaction corresponds to the reaction between **2** and Ag(PF<sub>6</sub>) described above. It cannot be quantitative in the present case, since only one equivalent of Ag<sup>+</sup> ions per two equivalents of compound **2** is released during the dissociation. It shall be noted that a similar behavior is observed for the Ag<sup>+</sup> bridged rhodium and iridium complexes of ref. 36.

## Conclusions

An unexpected oxidation of the technetium(I) complex [Tc(NO)(L<sup>OMe</sup>)(PPh<sub>3</sub>)Cl] (**2**) and the formation of the Tc(II) compound [Tc(NO)(L<sup>OMe</sup>)(PPh<sub>3</sub>)Cl](PF<sub>6</sub>) (**3**) are observed during reactions with Ag(PF<sub>6</sub>) in THF or CH<sub>2</sub>Cl<sub>2</sub>. The oxidation of the transition metal can partially be suppressed by the addition of SMe<sub>2</sub> in acetonitrile and a considerable amount of the dimeric complex [{Tc<sup>I</sup>(NO)(L<sup>OMe</sup>)(PPh<sub>3</sub>)Cl]<sub>2</sub>Ag}(PF<sub>6</sub>) (**4**) precipitates from the reaction mixture under such conditions. The dimer contains a central {Cl-Ag-Cl} bridge, which dissociates in solution under re-formation of the starting material.

## Experimental Section

**Materials.** All chemicals were reagent grade and used without further purification. The starting complex  $[\text{Tc}(\text{NO})(\text{L}^{\text{OMe}})(\text{PPh}_3)_2\text{Cl}]$  has been prepared by a published procedure.<sup>[22]</sup>

**Physical Measurements.** The IR spectra of were recorded on a Shimadzu FTIR 8300 spectrometer. NMR spectra were recorded at 298 K on JEOL ECS 400 or JEOL JNM-ECA400II spectrometers. EPR spectra were recorded for  $\text{CH}_2\text{Cl}_2$  solutions in the X-band at room temperature and at 78 K on a Magnetech Miniscope spectrometer. Simulations were done with Easyspin.<sup>[37]</sup>

**Radiation Precautions.**  $^{99}\text{Tc}$  is a long-lived  $\beta^-$  emitter ( $E_{\text{max}} = 0.292$  MeV). Normal glassware provides adequate protection against the weak beta radiation as long as milligram amounts of the samples are used. Secondary X-rays (bremsstrahlung) play a significant role only when larger amounts of  $^{99}\text{Tc}$  are handled. All manipulations were done in a laboratory approved for the handling of radioactive materials.

## Syntheses

$[\text{Tc}(\text{NO})(\text{PPh}_3)(\text{L}^{\text{OMe}})\text{Cl}](\text{PF}_6)$  (**3**).  $[\text{Tc}(\text{NO})(\text{PPh}_3)(\text{L}^{\text{OMe}})\text{Cl}]$  (17 mg, 0.02 mmol) was suspended in  $\text{CH}_2\text{Cl}_2$  (0.3 mL).  $\text{Ag}(\text{PF}_6)$  (5 mg, 0.02 mmol) was added and the mixture was stirred for 1 h at room temperature. The solvent was removed under vacuum and the residue was washed with toluene (5 mL) and pentane (5 mL). The residue was extracted with  $\text{CH}_2\text{Cl}_2$  and filtered to remove elemental silver.  $[\text{Tc}(\text{NO})(\text{PPh}_3)(\text{L}^{\text{OMe}})\text{Cl}](\text{PF}_6)$  was obtained as a dark red powder after complete evaporation of the solvent. Yield 9 mg (51%). Single crystals for X-ray diffraction were obtained from a  $\text{CH}_2\text{Cl}_2$ /pentane mixture. IR (KBr,  $\text{cm}^{-1}$ ): 1786 ( $\nu_{\text{NO}}$ ). EPR (78 K):  $A_{\perp}^{\text{Tc}} = 100 \cdot 10^{-4} \text{ cm}^{-1}$ ,  $A_{\parallel}^{\text{Tc}} = 247 \cdot 10^{-4} \text{ cm}^{-1}$ ,  $g_{\perp} = 2.015$ ,  $g_{\parallel} = 1.972$ . EPR (RT):  $g_0 = 2.0247$ ,  $a_0^{\text{Tc}} = 139.5 \cdot 10^{-4} \text{ cm}^{-1}$ .

$[\text{Tc}(\text{NO})(\text{PPh}_3)(\text{L}^{\text{OMe}})\text{Cl}]_2\text{Ag}(\text{PF}_6)$  (**4**).  $\text{Ag}(\text{PF}_6)$  (25 mg, 0.1 mmol) and  $\text{SMe}_2$  (0.5 mL) were added to a suspension of  $[\text{Tc}(\text{NO})(\text{PPh}_3)(\text{L}^{\text{OMe}})\text{Cl}]$  (88 mg, 0.1 mmol) in THF (1.5 mL). Acetonitrile (one drop) and  $\text{CH}_2\text{Cl}_2$  (two drops) were added after heating at 60 °C for 1 h. The resulting red solution was heated at 60 °C for another 3 h. The colorless precipitate ( $\text{AgCl}$ ) formed upon cooling to room temperature was filtered off. The filtrate was layered with diethyl ether (18 mL) and pentane (15 mL). Orange-red crystals of  $[\text{Tc}(\text{NO})(\text{PPh}_3)(\text{L}^{\text{OMe}})\text{Cl}]_2\text{Ag}(\text{PF}_6)$  (**4**) and red crystals of  $[\text{Tc}(\text{NO})(\text{PPh}_3)(\text{L}^{\text{OMe}})\text{Cl}](\text{PF}_6)$  (**3**) formed after storage of the mixture in a refrigerator for 72 h. The crystals were filtered off and extracted with toluene (2 x 5 mL). The solvent was removed in vacuum to give  $[\text{Tc}(\text{NO})(\text{PPh}_3)(\text{L}^{\text{OMe}})\text{Cl}]_2\text{Ag}(\text{PF}_6)$  as an orange-red powder. Single crystals of  $4 \cdot \text{CH}_2\text{Cl}_2$  were obtained from a  $\text{CH}_2\text{Cl}_2$ /toluene mixture. Yield 35 mg (38%). IR (KBr,  $\text{cm}^{-1}$ ): 1705 ( $\nu_{\text{NO}}$ ).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , ppm): 7.65–7.29 (m, 30H,  $\text{PPh}_3$ ), 4.98 (s, 10H, Cp), 3.88 (s, 18H,  $\text{OCH}_3$ ), 3.16 (s, 6H,  $\text{OCH}_3$ ), 2.89 (s, 6H,  $\text{CH}_3$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , ppm): 119.6 (s,  $\text{PO}(\text{OMe})_2$ ), -144.3 (sept,  $^1\text{J}_{\text{P-F}} = 715$  Hz,  $\text{PF}_6$ ).  $^{99}\text{Tc}$  NMR ( $\text{CDCl}_3$ , ppm): 2179 (s,  $\nu_{1/2} = 23.5$  kHz).

**X-ray Crystallography.** The intensities for the X-ray diffraction studies were recorded on a STOE IPDS T2 ( $3 \cdot \text{CH}_2\text{Cl}_2$ ) and a Bruker D8 Venture instrument ( $4 \cdot \text{CH}_2\text{Cl}_2$ ) with Mo  $K\alpha$  radiation ( $\lambda = 0.71073$  Å). The space groups were determined from systematic absences. Structure solutions and refinements were performed with the SHELX program package.<sup>[38,39]</sup> Absorption corrections were done with SADABS.<sup>[40]</sup> Hydrogen atoms were calculated for the idealized positions and treated with the 'riding model' option of SHELXL. The representation of molecular structures was done by the program

DIAMOND 4.<sup>[41]</sup> More details about the analyses are contained in the Supporting Information.

Deposition Numbers 2105101 ( $3 \cdot \text{CH}_2\text{Cl}_2$ ) and 2105102 ( $4 \cdot \text{CH}_2\text{Cl}_2$ ) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service [www.ccdc.cam.ac.uk/structures](http://www.ccdc.cam.ac.uk/structures).

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## Conflict of Interest

The authors declare no conflict of interest.

## Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

**Keywords:** Technetium · nitrosyl complexes · EPR · tripod ligands

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