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[Tc(NO)Cl(Cp)(PPh_3)] – A Technetium(I) Compound with an Unexpected Synthetic Potential

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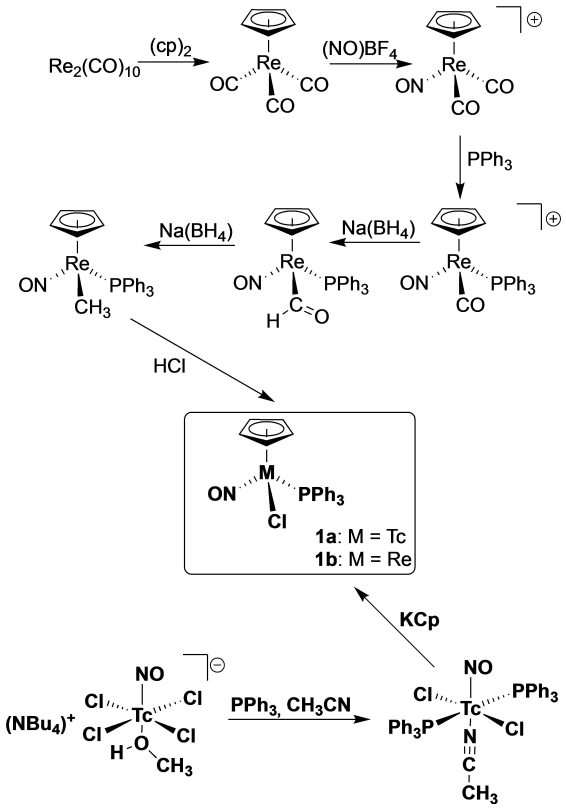
Reactions of the chiral organometallic technetium(I) compound [Tc(NO)Cl(Cp)(PPh_3)] (**1 a**) with phosphines and alkynes give unexpected products such as the dimeric cation [{Tc(NO)(Cp)(PPh_3)}$_2$Cl]$^+$ (**4**) or the Fischer-type carbene [Tc(NO)(Cp)(PPh_3){C(OR)$C_2H_4PPh_3$}]$^{2+}$ (**5**). Both products could be isolated as PF_6^- salts and studied by spectroscopic methods and X-ray diffraction. While [Tc(NO)(Cp)(PMe_3)(PPh_3)](PF_6) (**2**PF_6) can be obtained from **1 a**, PMe_3 and Ag(PF_6) under ambient conditions, the synthesis of the corresponding bis-triphenylphosphine complex [Tc(NO)(Cp)(PPh_3)$_2$](PF_6) (**3**PF_6) requires high temperatures and long reaction times. The products are stable in air.

Introduction

The gamma-emitting nuclide ^{99m}Tc (E_γ = 0.143 MeV, $t_{1/2}$ = 6.01 h) is widely used in diagnostic nuclear medicine with currently about 40 million annual administrations in more than 10,000 hospitals worldwide.[1–5] It can potentially be combined with the beta-emitting rhenium isotope ^{188}Re (E_{max} = 2.12 MeV, $t_{1/2}$ = 17.02 h) in theranostic preparations.[6–8] This, however, requires an exact knowledge of the related chemistry of the two elements. Particularly bioorganometallic approaches entered the center in interest during the recent years,[9–12] which draws special attention to the hitherto only poorly developed organotechnetium chemistry,[13] while that of rhenium can be regarded as comparatively well explored.[14]

The focus of the related research has been set to bis(arene) complexes and cyclopentadienyl (Cp^-) compounds.[15–20] Both type of compounds can be readily substituted on their aromatic rings and, thus, give access to conjugation with biological vectors as has been demonstrated for a number of examples. Almost all of these cyclopentadienyl derivatives are tricarbonyltechnetium(I) complexes. This has to do with the ready availability of ^{99m}Tc and ^{99}Tc precursors with the {Tc(CO)$_3$}$^+$ core.[21,22]

Other Cp^- complexes of technetium are only poorly explored. This also includes nitrosyl compounds, which represent a large family of complexes in the chemistry of the heavier congener rhenium. Complexes of the compositions [Re(NO)(L)(Cp)(PPh_3)]$^{0,+}$, where L represents a large variety of ligands, are known for many years and a fascinating chemistry has been established comprising more than 100 papers and 200 crystal structures.[23–34] However, a key complex of this class of compounds, [Re(NO)Cl(Cp)(PPh_3)] (**1 b**), is synthesized in a multiple-step synthesis starting from $Re_2(CO)_{10}$ (Scheme 1), which is less favored for the radioactive element technetium.



Scheme 1. Synthesis of [M(NO)(Cp)Cl(PPh_3)] complexes (M=Tc, Re).

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Recently, we reported a simple two-step approach to [Tc(NO)Cl(Cp)(PPh_3)] (**1 a**),[34] using the common starting material (NBu_4)[Tc(NO)Cl_4] (Scheme 1), which may have opened the door to the related technetium chemistry. Indeed, the chloride ligand of **1 a** can be replaced by other halides, pseudohalides or related ligands, but also the cationic carbonyl complex [Tc(NO)(CO)(Cp)(PPh_3)](PF_6) has been prepared by subsequent treatment of **1 a** with Ag(PF_6) and CO gas as has been shown in initial experiments.[34,35]

Results and Discussion

In continuation of the successful reactions of the chiral complex **1 a** with carbon monoxide,[34] we tried to apply the procedure to reactions with other neutral ligands such as phosphines and alkynes. Following the reported protocol,[34] we added stoichiometric amounts of Ag(PF_6) as chloride scavenger and source for an appropriate counter anion. As can be derived from Scheme 2, which contains a summary of the performed experiments, some of the reactions were not straightforward and gave unexpected results.

The anticipated ligand-exchange product [Tc(NO)(Cp)(PMe_3)(PPh_3)]$^+$ (**2**) was obtained from the reaction of **1 a** with PMe_3 and Ag(PF_6) in CH_2Cl_2 under moderate conditions. The progress of the reaction can be followed by a color change from deep red to orange-yellow and the precipitation of some AgCl. The completion of the reaction is indicated by the disappearance of the ^{99}Tc NMR signal of the starting material at −235 ppm in the reaction mixture and the appearance of the product signal at −1420 ppm. Besides the septet of the PF_6^- counter ion, the ^{31}P NMR spectrum of the product shows two resonances at 32.1 (coordinated PMe_3) and 27.9 ppm (coordinated PPh_3). They are surprisingly narrow and well resolved, which is not common for ^{31}P NMR spectra of technetium compounds, where frequently an extreme line-broadening is observed due to scalar couplings between the ^{31}P and ^{99}Tc nuclei.[36,37]

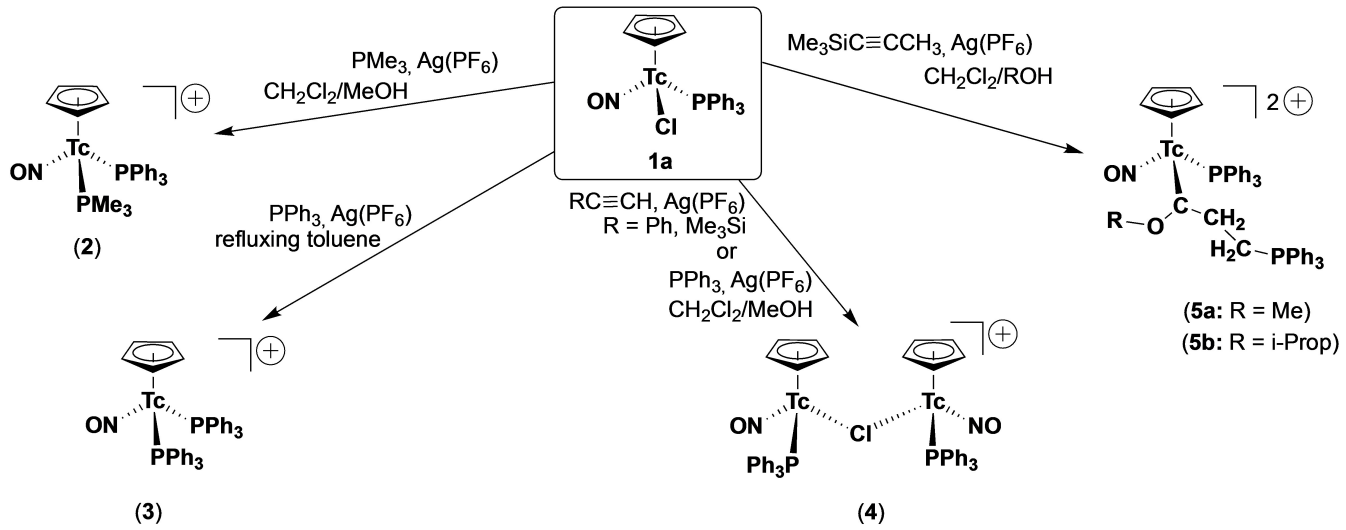
Table 1. Selected bond lengths (Å) and angles (°) in [Tc(NO)(Cp)(PMe_3)(PPh_3)]$^+$ (**2**), [Tc(NO)(Cp)(PPh_3)$_2$]$^+$ (**3**) and [{Tc(NO)(Cp)(PPh_3)}$_2$Cl]$^+$ (**4**).

	2	**3**[a]	**4**
Tc–N10	1.766(5)	1.765(3)/1.758(4)	1.75(1)
Tc–P1	2.383(1)	2.390(1)/2.4331(9)	2.368(3)
Tc–P2/Cl	2.390(2)	2.4082(9)/2.4233(1)	2.427(2)
N10–O10	1.177(7)	1.184(4)/1.758(4)	1.19(1)
Tc–N10–O10	175.6(5)	173.7(3)/173.6(3)	177(1)
N10–Tc–P1	94.1(2)	91.1(1)/93.6(1)	91.0(3)
N10–Tc–P2/Cl	92.9(2)	97.9(1)/97.5(1)	97.9(3)
P1–Tc–P2/Cl	95.50(5)	97.76(3)/97.47(3)	86.1(1)
Tc–Cl–Tc′	–	–	115.4(2)

[a] Values for two independent species. Symmetry operation (′): 1-x, y, 1.5-z.

Yellow single crystals of [Tc(NO)(Cp)(PMe_3)(PPh_3)](PF_6) were obtained from CH_2Cl_2/diethyl ether. The IR spectrum of the product shows the $\nu_{(NO)}$ stretch as an intense band at 1718 cm^{-1}. This value is at a significantly higher frequency compared with that of **1 a** (1682 cm^{-1}) and a clear sign of the replacement of Cl^- by a ligand with π-acceptor properties, which lowers the degree of back-donation into anti-binding orbitals of the nitrosyl ligand.

[Tc(NO)(Cp)(PMe_3)(PPh_3)](PF_6) crystallizes as racemate in the centrosymmetric space group C2/c. Figure 1a shows the molecular structure of the mixed-phosphine complex. Selected bond lengths and angles are summarized in Table 1. The Tc–N10–O10 angle is 175.6(5)° and confirms the assumption of a linear NO^+ ligand as has been found for all hitherto structurally characterized nitrosyl complexes of technetium.[33,38] The P–Tc–N and P–Tc–P angles in the pseudo-tetrahedral complex are between 92.9(2) and 95.50(5) Å. Similar rhenium complexes have been prepared by reactions of [Re-



Scheme 2. Performed reactions and their products.

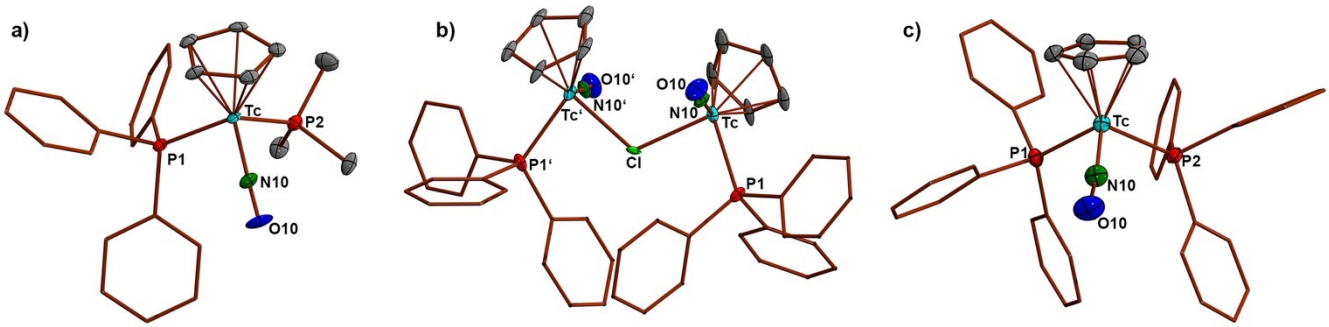


Figure 1. Structures of the complex cations a) $Tc(NO)(Cp)(PMe_3)(PPh_3)]^+$ (**2**), b) $[\{Tc(NO)(Cp)(PPh_3)\}_2Cl]^+$ (**4a**) and c) $[Tc(NO)(Cp)(PMe_3)(PPh_3)]^+$ (**3**). Ellipsoids are depicted at 50% probability. Hydrogen atoms are omitted for clarity.

$(NO)(Cp)(X)(PPh_3)]$ complexes (X = tosylate or triflate) with the secondary phosphines PPh_2H, PEt_2H, PBu_2H. A subsequent treatment of the obtained phosphine complexes with potassium butanolate gave access to the related phosphide complexes.[39,40]

Having in mind that a related rhenium complex with two PPh_3 ligands has successfully been prepared by the treatment of $[Re(NO)(Cp)(CO)(PPh_3)]^+$ with $(CH_3)_3N^+O^-$ in the presence of PPh_3,[41] we also attempted the reaction of $[Tc(NO)(Cp)Cl(PPh_3)]$ (**1a**) with PPh_3 and $Ag(PF_6)$ following the well-functioning protocol described above for PMe_3. We observed the precipitation of some AgCl, but surprisingly, there was no evidence for the formation of a bis-triphenylphosphine complex. The ^{99}Tc NMR spectrum of the reaction mixture showed only a marginal shift of the signal of the starting compounds from −235 ppm to −220 ppm. This should definitively not be indicative for an exchange of the chlorido ligand by a phosphine, particularly with regard to the change of the ^{99}Tc chemical shift by more than 1000 ppm upon the Cl^-/PMe_3 exchange. And indeed, a single crystal structure determination on the red crystals, which could be isolated from the reaction mixture, confirmed the formation of the dimeric complex $[\{Tc(NO)(Cp)(PPh_3)\}_2Cl](PF_6)$ (**4**PF_6). The structure of the complex cation is depicted in Figure 1b and selected bond lengths and angles are given in Table 1. They are very similar to the values in the parent compound **1a**, and also the Tc–Cl bond of 2.427(2) Å is only slightly longer than the value in the monomeric compound **1a** (2.412(2) Å).[42] The $[\{Tc(NO)(Cp)(PPh_3)\}_2Cl]^+$ cation is the first example of a complex having a single chlorido bridge between two technetium atoms. The non-restrained Tc–Cl–Tc' angle of 115.4(2) Å is clearly larger than those in $[\{TcCl(NO)(CO)_2\}_2(\mu\text{-}Cl)_2]$ (96.5°) or $(NBu_4)[\{Tc(CO)_3\}(\mu\text{-}Cl)_3]$ (81.6°),[43,44] but in agreement with the Re–I–Re angle of 114.14(4)° in the analogous rhenium compound $[\{Re(NO)(Cp)(PPh_3)\}_2I](BF_4)$.[45] Structural data for the chlorido-bridged rhenium compound are not available.

Since there is no consumption of PPh_3 during the formation of this product and also only 0.5 equivalents of Ag^+ ions are required, it is also formed when no extra PPh_3 is added and smaller amounts of $Ag(PF_6)$ are used. Moreover, the cationic complex **4** seems to be formed whenever the chlorido ligand of **1a** is abstracted (e.g. during the interaction with Ag^+ ions) and no suitable additional ligand is present for the stabilization of the formed fragment (see also the attempted reactions outlined *vide infra*). The formation of the dimeric species seems to be fast and avoids the complete removal of Cl^- by the added Ag^+ ions. One of the possible explanations of the obvious resistance of this compound against further exchange reaction might be the steric shielding of the central Tc–Cl–Tc' unit. Figure 2 visualizes the steric bulk around the central ligand. The strong shielding of the metal atoms in **4** suggests that a cleavage of the Tc–Cl bonds in this 'kinetic' product or a fast ligand exchange is a prerequisite for the formation of monomeric products as can be provided by an elevated temperature.

And indeed, a reaction between **1a**, $Ag(PF_6)$ and PPh_3 in boiling toluene gave the desired product $[Tc(NO)(Cp)(PPh_3)_2](PF_6)$ (**3**) in moderate yields. In analogy to the reaction with PMe_3 described above, the progress of the reaction can be observed by a color-change from deep red to orange yellow and a significant shift of the ^{99}Tc NMR signal from −235 ppm to −1219 ppm.

Single crystals of **3** were obtained from CH_2Cl_2/toluene and could be studied by X-ray diffraction. A plot of the structure is shown in Figure 1c and selected bond lengths and angles are compared with the values of **2** and **4** in Table 1. The bonding parameters are unexceptional and indicate that the presence of two PPh_3 ligand in the coordination sphere of technetium does not induce a significant steric stress.

Attempted reactions of **1a** with alkynes gave surprising results, particularly in the light that the corresponding rhenium Lewis acid $[Re(NO)(Cp)(PPh_3)]^+$ shows an extended chemistry

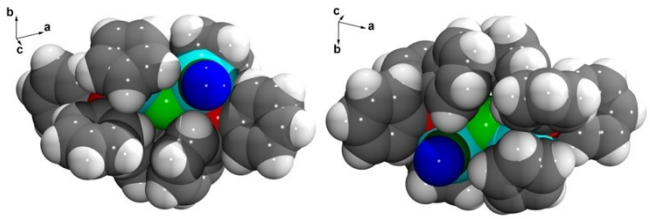


Figure 2. Space-filling model of the complex cation of $[\{Tc(NO)(Cp)(PPh_3)\}_2Cl](PF_6)$.

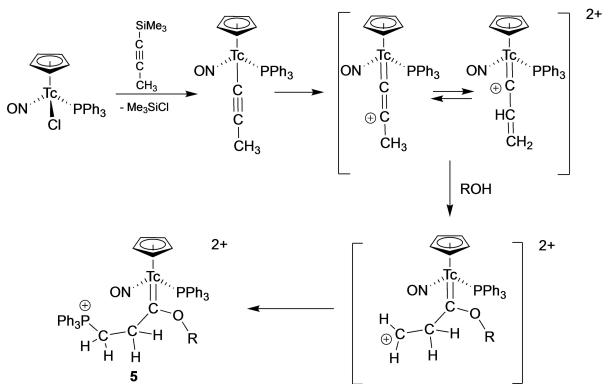
with such ligands and many complexes with side-on bonded alkynes or end-on bonded acetylides have been isolated, extensively studied and structurally characterized.[33,46,47] The treatment of **1a** with symmetric alkynes such as butyne or hexyne did not show any reaction irrespective of the conditions applied. Even in neat alkynes, no reaction was observed, which could readily be detected by ^{99}Tc NMR spectroscopy. As the sole product of such attempts, [{Tc(NO)(Cp)(PPh_3)}$_2$Cl](PF_6) could be isolated from such solutions after addition of Ag(PF_6). These results underline the statement made above that the dimeric compound is formed whenever no suitable other ligand is available.

Surprising results were obtained from attempted reactions of **1a** with trimethysilyl acetylene or trimethylsilyl propyne. The intensity of the ^{99}Tc NMR signal of the starting material gradually disappeared and new signals became soon visible at −1375 and −1372 ppm. However, in the course of the reaction a number of additional Tc(I) compounds are formed. Despite several attempts under various conditions, we failed in the isolation of the assumed alkyne or alkynide complexes. But finally, a few brown crystals of an unexpected carbene complex, [Tc(NO)(Cp)(PPh_3){C(OMe)$C_2H_4PPh_3$}](PF_6)$_2$ (**5a**) could be isolated from a reaction of **1a** with Ag(PF_6) and trimethylsilyl propyne in a toluene/MeOH mixture. Considering the composition of this product as a carbene, the synthesis could be optimized by increasing the amount of added methanol, which has originally only be use to partially dissolve Ag(PF_6). Yields of approximately 20% were obtained for **5a**. Interestingly, they could not be increased by the addition of an extra equivalent of PPh_3, which should clearly support the formation of the obtained phosphonio compound. These findings suggest a complex mechanism for the formation of **5a**, during which the release of PPh_3 from **1a** or **2** is sufficient and a number of other, hitherto not structurally identified product seem to play a role. This is not completely surprising in the light that various species such as alkyne and alkynides, vinylidene and carbene complexes should be reactive intermediates in the formation of **5a**. Some of them are shown in Scheme 3. It should be mentioned that a similar reaction is also observed with iso-propanol instead of MeOH giving a product (**5b**) with an ^{99}Tc NMR signal at −1370 ppm and an ^{31}P NMR spectrum, which is practically identical with that of **5a**.

A very limited number of similar reactions and compounds have been reported previously. The formation of Fischer-type carbenes of the composition [Re(NO)(Cp)(PPh_3){C(OMe)R}] (R=Me, Ph) has been observed during reactions of acyl complexes with $MeSO_3F$,[49] and also some analogous manganese complexes are known.[50] Additionally, there exist two related platinum compounds, which are formed from H_2PtCl_6, when it is treated with $Me_3SiCH_2C{\equiv}CH$ or $Me_3SiC{\equiv}CH$ in iso-propanol.[51,52]

Compound **5a**, is one of the very few Fischer-type carbenes of technetium und only the second that has been isolated in crystalline form and studied by X-ray diffraction. The only other one, [Tc(Cp*)(CO)$_2${C(Ph)OEt}], has been prepared by *Fischer et al.* following the classical route by the subsequent treatment of a [Tc(Cp*)(CO)$_3$] with LiPh and (Et_3O)(BF_4).[48] In addition to the metal-driven formation of a carbene from an alkyne and an alcohol, the isolated product **5a** shows another remarkable feature: the addition of PPh_3 and the formation of an alkylphosphonio substituent, which finally leads to a doubly charged organometallic cation. The presence of the phosphonio unit is evident from the appearance of an additional broad ^{31}P NMR signal at 11 ppm. Similar products, alkenylphosphonio complexes of ruthenium (with related ^{31}P resonances around 17 ppm), have been obtained from reactions of vinylidene complexes with PPh_3, and corresponding alkyne species were discussed as possible intermediates.[53,54] For the formation of **5a**, there is currently no sufficient information available to derive a well-justified mechanism for its formation, but we suppose that species as shown in Scheme 3 play a role. For the given sequence, however, is not yet any experimental proof and also the initial formation of a side-on bonded alkyne complex with subsequent shift and cleavage of the trimethylsilyl substituent seems to be possible. A deeper mechanistic survey is hindered by the radioactivity of technetium and the fact that similar reactions seem not to proceed with rhenium, where the formation of stable alkyne and alkynido complexes is preferred.[43,46,47]

Figure 3 depicts the structure of the complex cation of **5a** and selected bond lengths and angles are summarized in Table 2. The nitrosyl ligand is linearly bonded and, thus, must be regarded as a formal NO^+ as in the other complexes of this study. The Tc–C(11)$_{carbene}$ bond of 2.013(4) Å is only slightly longer than the value in [Tc(Cp*)(CO)$_2${C(Ph)OEt}] (1.97(2) Å),[48]



Scheme 3. Intermediates assumed to play a role in the formation of **5**.

Table 2. Selected bond lengths (Å) and angles (°) in [Tc(NO)(Cp)(PPh_3){C(OMe)$C_2H_4PPh_3$}]$^{2+}$ (**5a**).

Tc–N10	1.776(4)	O1–C9	1.439(4)
Tc–P1	2.398(1)	C6–C7	1.528(5)
Tc–C6	2.013(4)	C7–C8	1.531(5)
N10–O10	1.168(4)	C8–P2	1.804(4)
C6–O1	1.303(4)		
Tc–N10–O10	174.7(3)	Tc–C6–C7	121.6(2)
N10–Tc–P1	87.6(1)	C6–O1–C9	123.8(3)
N10–Tc–C6	97.8(2)	C6–C7–C8	114.0(3)
P1–Tc–C6	91.1(1)	C7–C8–P2	113.1(3)
Tc–C6–O1	131.7(3)		

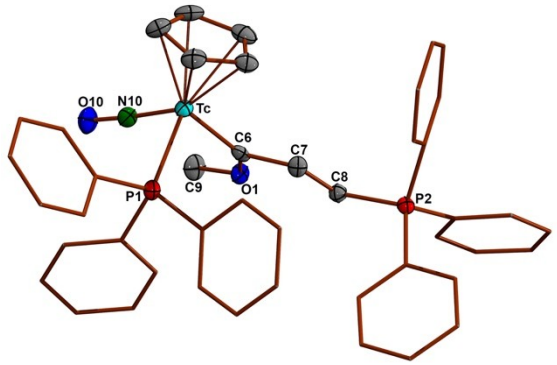


Figure 3. Structure of the $[Tc(NO)(Cp)(PPh_3)\{C(OMe)C_2H_4PPh_3\}]^{2+}$ cation (**5a**). Ellipsoids are depicted at 50% probability. Hydrogen atoms are omitted for clarity.

but clearly longer than in the vinylidene complex $[Tc(dppe)_2Cl\{=C=C(H)Ph\}]$ (1.861(9) Å).[55] The C6–C7 and C7–C8 bonds are in the normal range of single bonds, which excludes the formation of an alkenylphosphonio moiety as in the ruthenium compounds of ref. 54.

^{99}Tc NMR spectroscopy has been proven as a valuable method for the evaluation of reactions starting from the Tc(I) complex $[Tc(NO)Cl(Cp)(PPh_3)]$ (**1a**). Although the resonances are extremely broad with half-line widths between 4100 (**2**) and 7200 Hz (**1a**), the signals of the individual compounds are well-separated with respect to the large chemical shift range of more than 11,000 ppm, in which ^{99}Tc NMR resonances appear.[56] Even the signals of Tc(I) nitrosyl complexes span a chemical shift range from +2017 ppm for $[Tc(NO)(NH_3)_4(OOCCF_3)]^+$ to −1753 ppm for $[Tc(NO)(Cp)(CO)(PPh_3)]^+$.[34,57] There seems to a be a clear dependence of the chemical shift on the donor/acceptor properties of the coordinated ligands: strong donors such as NH_3 cause downfield shifts, while acceptor ligands such as CO shift the ^{99}Tc NMR signal upfield.[57] This is also observed for the compounds of this study, where complexes **1a** and **4** (in which the metal has the identical 'Cp/NO/PPh_3/Cl coordination sphere') have almost identical chemical shifts of −235 and −220 ppm. The replacement of the Cl^- ligand by phosphines causes an upfield shift by 1500 ppm. In the same range (between −1200 and −1450 ppm), the signals of the Fischer-type carbenes are observed.

Conclusions

A number of remarkable products were observed during reactions of $[Tc^I(NO)(Cp)Cl(PPh_3)_2]$ (**1a**) with phosphines and alkynes. The dimeric compound $[\{Tc^I(NO)(Cp)(PPh_3)\}Cl]^+$ (**4**) is formed whenever the Cl^- ligand is removed from **1a** without providing a suitable incoming ligand. Complexes with Fischer-type ligands are the products when **1a** is exposed to alkynes with a terminal trimethylsilyl group in the presence of an alcohol.

The formation of such stable carbene complexes reflects a considerable potential of technetium for the activation of small molecules. Similar observations have been made recently in a study about hydrido complexes.[58] This aspect of the technetium chemistry has hitherto only occasionally been addressed,[59–61] which may be perspicuous with regard to the radioactivity of all isotopes of this element.

The title compound shows reactivities clearly different from the chemistry of its rhenium analog. We regard this as an important aspect, which relativizes the paradigm of an identical behavior of the two elements.

Another remarkable point is the stability of the organometallic compounds obtained. Given that such unusual reactions can also be performed with the short-lived isotope ^{99m}Tc, they are also interesting for the nuclear medical aspect of technetium chemistry.

Experimental Section

All chemicals used in this study were reagent grade and used without further purification. Solvents were dried and distilled prior to use. ^{99}Tc was purchased as solid ammonium pertechnetate from Oak Ridge National Laboratory (ORNL) and purified as published previously.[57] $[Tc(NO)Cl_2(PPh_3)_2(MeCN)]$, $(NBu_4)[Tc(NO)Cl_4(MeOH)]$ and $[Tc(NO)Cl(Cp)(PPh_3)]$ were prepared as described in the literature.[34,62,63] KCp was obtained following the procedure of Roesky et al.[64]

IR spectra were measured from KBr pellets on a Shimadzu FTIR 8300 spectrometer between 400 and 4000 cm^{-1}. NMR spectra were recorded on a JEOL 400 MHz spectrometer, which corresponds to a ^{99}Tc frequency of 90.063 MHz. The ^{99}Tc chemical shifts refer to a solution $NaTcO_4$ in D_2O.

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

Single crystal X-ray diffraction data were collected on a Bruker D8 Venture instrument. Absorption corrections were carried out by the multiscan (SADABS) method.[65] Structure solutions and refinements were done with the SHELX-2008, SHELX-2014 and SHELX-2016 program packages.[66,67] Hydrogen atom positions were placed at calculated positions and refined by a riding model. More details about data collection and refinement procedures are provided together with full lists of bond lengths and angels in the Supporting Information. The visualization of the molecular structures was done using the program DIAMOND 4.2.2.[68]

$[Tc^I(NO)(Cp)(PPh_3)(PMe_3)](PF_6)$ (2PF_6). $[Tc(NO)Cl(Cp)(PPh_3)]$ (50 mg, 0.1 mmol) was dissolved in 10 mL CH_2Cl_2 and treated with a solution of $AgPF_6$ (25 mg, 0.1 mmol) in 2 mL CH_2Cl_2/MeOH (2/1, v/v). Trimethylphosphine (0.5 mL) was added to the reaction mixture, which was heated under reflux for 4 h. The solution was filtered and the solvent was removed under vacuum. The residue was dissolved in 1 mL CH_2Cl_2 and covered with 4 mL diethyl ether. Yellow crystals were formed after diffusion of the solvents. Yield 47% (38 mg). IR (KBr, cm^{-1}): 3442 (w), 2968 (w), 2932 (w), 1734 (vs), 1479 (w), 1431 (m), 1292 (m), 1093 (m), 952 (s), 840 (vs), 746 (m), 696 (m), 555 (s), 522(w), 499 (w). ^{1}H NMR ($CDCl_3$, ppm): 7.14–7.31 (m, 15H, Ph), 5.17 (s, 5H, Cp), 1.44 (d, 9H, PMe_3). ^{13}C NMR ($CDCl_3$,

ppm): 128–131.7 (Ph), 93.2 (Cp). ^{31}P NMR ($CDCl_3$, ppm): 32.1 (s, PMe_3), 27.9 (s, PPh_3), 147 (m, PF_6). ^{99}Tc NMR ($CDCl_3$, ppm): −1420 ($\nu_{1/2}$ = 4100 Hz).

[Tc^{I}(NO)(Cp)(PPh$_3$)$_2$](PF$_6$) (3PF$_6$). [Tc(NO)Cl(Cp)(PPh_3)] (50 mg, 0.1 mmol) was dissolved in 10 mL CH_2Cl_2/toluene (5:95, v/v) and treated with a solution of $AgPF_6$ (25 mg, 0.1 mmol) in 2 mL CH_2Cl_2/MeOH (2/1, v/v). Triphenylphosphine (40 mg, 0.15 mmol) was added to the reaction mixture, which was heated under reflux for 6 h. The solution was filtered and the solvent was removed under vacuum. The residue was dissolved in 1 mL CH_2Cl_2 and covered with 3 mL toluene. Orange-red crystals were formed after diffusion of the solvents. Yield 45% (39 mg). IR (KBr, cm^{-1}): 3402 (w), 3055 (w), 2960 (s), 2924 (m), 2852 (w), 1716 (s), 1481 (w), 1435 (m),1307 (w), 1261 (vs), 1186 (m), 1116 (vs), 1091 (vs), 1024 (s), 839 (s), 804 (s), 750 (m), 721 (m), 694 (s). ^{1}H NMR ($CDCl_3$, ppm): 7.14–7.67 (m, 30H, Ph), 5.18 (s, 5H, Cp). ^{31}P NMR ($CDCl_3$, ppm): 22.4 (s, PPh_3), 150 (m, PF_6) ^{99}Tc NMR ($CDCl_3$, ppm): −1219 ($\nu_{1/2}$ = 6600 Hz). The resonances in the ^{13}C NMR spectra were of low intensities and no accurate values could be assigned.

[{Tc^{I}(NO)(Cp)(PPh$_3$)}Cl](PF$_6$) (4PF$_6$). [Tc(NO)Cl(Cp)(PPh_3)] (50 mg, 0.1 mmol) was dissolved in 10 mL CH_2Cl_2 and treated with a solution of $AgPF_6$ (25 mg, 0.1 mmol) in 2 mL CH_2Cl_2/MeOH (2/1, v/v). A dark grey precipitate was formed. The reaction mixture was stirred at room temperature for 5 h. The solution was filtered and the solvent was removed under vacuum. The residue was extracted with 1 mL CH_2Cl_2 and the obtained solution was covered with 3 mL diethyl ether. Red crystals were formed after slow diffusion of the solvents. Yield 44% (48 mg). IR (KBr, cm^{-1}): 3429 (w), 2924 (w), 1685 (vs), 1481 (w), 1435 (s), 1311 (w), 1222 (w), 1182 (m), 1122 (m), 1093 (m), 1066 (w), 840 (vs), 748 (m), 694 (s), 553 (m), 528 (s), 503 (m). ^{1}H NMR (CD_2Cl_2, ppm): 7.53–7.59 (m, 9H, Ph), 7.39–7.46 (m, 6H, Ph), 5.29 (s, 5H, Cp). ^{31}P{^{1}H} NMR (CD_2Cl_2, ppm): 29.0 (s, PPh_3), 144.5 (m, PF_6). ^{99}Tc NMR (CD_2Cl_2, ppm): −220 ($\nu_{1/2}$ = 4150 Hz). The resonances in the ^{13}C NMR spectra were of low intensities and no accurate values could be assigned.

[Tc^{I}(NO)(Cp)(PPh$_3$){C(OMe)C$_2$H$_4$PPh$_3$}](PF$_6$)$_2$ (5 a(PF$_6$)$_2$). [Tc(NO)Cl(Cp)(PPh_3)] (50 mg, 0.1 mmol) was dissolved in 5 mL toluene and treated with a solution of $AgPF_6$ (37 mg, 0.15 mmol) in 1 mL CH_2Cl_2/MeOH (2/1, v/v). 1-Trimethylsilylpropyne (0.25 mL, 1.5 mmol) was added to the deep red solution and the reaction mixture was stirred at room temperature for 6 h. The solution was filtered and the solvent was removed under vacuum to give a brown residue, which was dissolved in a small quantity of CH_2Cl_2 and chromatographed on silica gel. Elution with hexane/CH_2Cl_2 (1/2, v/v) resulted in the separation of an orange-red band containing the carbene complex. After the evaporation of the solvent, the residue was dissolved in 1 mL CH_2Cl_2 and covered with 4 mL toluene. Brown crystals were formed. Yield: about 19% (25 mg). IR (KBr, cm^{-1}): 3440 (w), 2924 (w), 1716 (vs), 1479 (m), 1435 (s), 1309 (m), 1120 (s), 1093 (s), 1026 (w), 999 (w), 839 (vs), 748 (m), 694 (s), 530 (s), 503 (w). ^{31}P{^{1}H} NMR ($CDCl_3$, pm): 29.2 (s, PPh_3), 11.2 (broad, PPh_3^+), 144.6 (m, PF_6). ^{99}Tc NMR ($CDCl_3$, ppm): −1371 ($\nu_{1/2}$ = 3900 Hz). High quality ^{1}H and ^{13}C NMR spectra of the pure product could not be obtained, since minor traces of the dimer complex could not be removed.

Deposition Numbers 2083770 (for [Tc(NO)(Cp)(PMe_3)(PPh_3)](PF_6)), 2083771 (for [{Tc(NO)(Cp)(PPh_3)}$_2$Cl](PF_6)×CH_2Cl_2), 2083772 (for Tc(NO)(Cp)(PPh_3){C(OMe)C$_2$H$_4$PPh$_3$}](PF_6)$_2$), and 2083773 (for [Tc(NO)(Cp)(PMe_3)(PPh_3)](PF_6)×0.75 toluene) 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.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: Carbenes · Dimers · Organometallics · Phosphonio ligands · Technetium

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