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Structural and Redox Variations in Technetium Complexes Supported by *m*-Terphenyl Isocyanides

Guilhem Claude, Federico Salsi, Adelheid Hagenbach, Milan Gembicky, Michael Neville, Chinglin Chan, Joshua S. Figueroa,* and Ulrich Abram*

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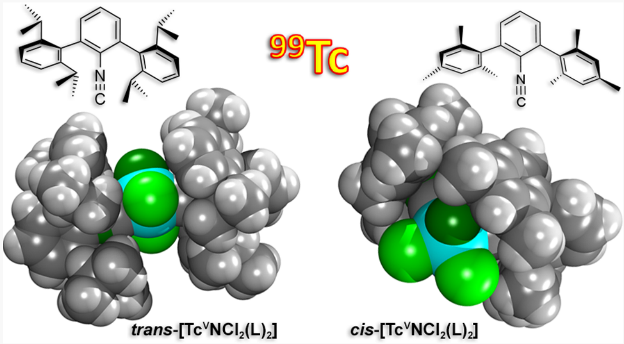
ABSTRACT: A series of technetium complexes with the sterically encumbered *m*-terphenyl isocyanides $CNAr^{Dipp2}$ (Dipp = 2,6-diisopropylphenyl) and $CNAr^{Mes2}$ (Mes = 2,4,6-trimethylphenyl) has been prepared. The products span three different oxidation states (+1, +3, and +5) of the radioactive transition metal and comprise carbonyl, nitrosyl, chloride, and nitrido complexes. All members of this series (*trans,mer*-$[Tc^{I}(CO)_3Cl(CNAr^{Dipp2})]$, *trans*-$[Tc^{I}(NO)Cl_2(PPh_3)(CNAr^{Dipp2})_2]$, $[Tc^{III}Cl_3(PMe_2Ph)_2(L)]$ (L = $CNAr^{Dipp2}$, $CNAr^{Mes2}$), *trans*-$[Tc^{V}NCl_2(CNAr^{Dipp2})_2]$, *cis*-$[Tc^{V}NCl_2(CNAr^{Mes2})_2(L)]$ (L = H_2O, MeOH), *cis*-$[Tc^{V}NBr_2(CNAr^{Mes2})_2]$, and *trans*-$[Tc^{V}(NPh)X_2(CNAr^{Dipp2})_2]$ (X = Cl, Br)) are stable under ambient conditions. The ν_{CN} IR frequencies measured for the complexes frequently appear at wavenumbers higher than those for the uncoordinated isocyanides, which suggests a low degree of back-donation into the CN π^* orbitals of these ligands.

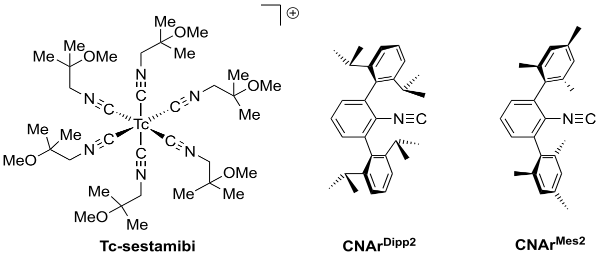


■ INTRODUCTION

The metastable nuclear isomer ^{99m}Tc (E_γ = 141 keV, $t_{1/2}$ = 6 h) remains the workhorse in routine diagnostic nuclear medicine.[1−4] Approximately 80% of all clinical imaging procedures in nuclear medicine are done with this SPECT (single photon emission computed tomography) isotope, which comprises about 40 million annual studies.[5]

From a chemical point of view, the transition metal technetium is not an optimal candidate for such a widespread application, since a direct labeling of organic molecules (such as with $^{123/131}I$ or the PET isotope ^{18}F)[6−8] is not possible. However, the outstanding radiation properties of ^{99m}Tc, its almost perfect half-life in the context of diagnostic imaging applications, and its permanent availability at the clinical site via a generator system will make this nuclide difficult to replace in the coming decade. In all cases of technetium radiopharmaceuticals, the synthesis of stable or kinetically inert coordination compounds is required in order to avoid *in vivo* ligand-exchange reactions with plasma components. Commonly, stabilization is achieved by the use of ligand systems with a high denticity. This means that chelators with a denticity of 3 or larger provide the required stabilization in SPECT radiopharmaceuticals such as ^{99m}Tc-MAG3, ^{99m}Tc-HMPAO, or the members of the ^{99m}Tc-IDA family.[1−4] An impressive example of kinetic stabilization is the myocardial-imaging agent ^{99m}Tc-sestamibi, or Cardiolite (Chart 1), in which six monodentate isocyanide ligands are stabilized by the d^6 electronic configuration of Tc(I).[9−13] Another concept for the stabilization of metal complexes and the prevention of subsequent ligand-exchange processes, which has hitherto only rarely been considered in nuclear medical imaging, is the use of sterically encumbered ligand systems.

Chart 1. Tc-sestamibi and Ligands Used throughout This Work



For all three approaches, an exact knowledge of the coordination chemistry of the radioactive transition metal is the foundation for the development of novel technetium-based tracer molecules. The corresponding structural studies are commonly done with the long-lived isotope ^{99}Tc, a weak β^--emitter (E_{max} = 0.294 MeV) with a half-life of 211100 years.

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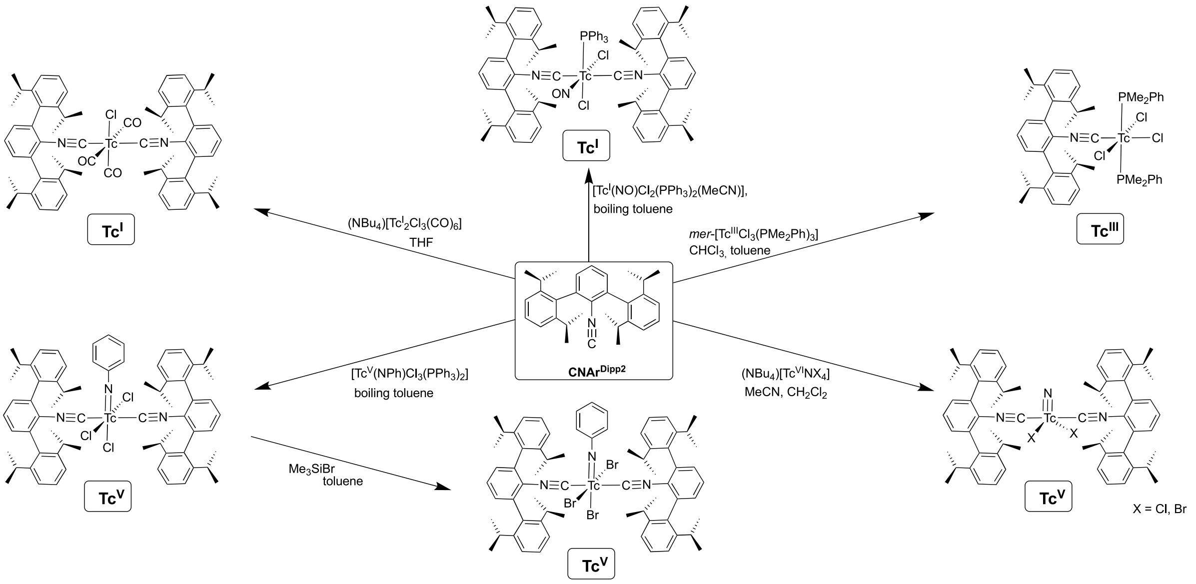
Scheme 1. Reactions Performed with $CNAr^{Dipp2}$



Over the past several years it has been demonstrated that *m*-terphenyl isocyanides are a useful class of ancillary ligands for the isolation of unusual and highly reactive transition-metal complexes.[14−23] These encumbering ligands are particularly adept at stabilizing transition-metal centers featuring high degrees of coordinative and electronic unsaturation. In addition, the kinetic protection afforded by *m*-terphenyl isocyanides has also allowed for the isolation of transition-metal complexes featuring unusual ligands such as boron monofluoride (BF) and nitrous oxide (N_2O).[24,25] An important feature of isocyanide ligands is their ability to function as both strong σ donors and π acids.[26,27] This dual property allows isocyanides to bind well to transition metals in a range of formal oxidation states. It has been previously reported that *m*-terphenyl isocyanides can stabilize unusual low-valent complexes of both manganese and molybdenum,[20,28−31] the chemistry of which often mirrors that of low-valent technetium complexes. However, some medium- to high-valent *m*-terphenyl isocyanide complexes of Mn and Mo have also been isolated via chemical oxidation of low-valent precursors,[28,32−34] thereby demonstrating the utility of these encumbering ligands across a range of metal-based redox states.

Given this precedent, we report here an initial survey of the coordination capabilities of *m*-terphenyl isocyanides to technetium. To assess the structural diversity available for this coordination platform, we have employed the *m*-terphenyl isocyanide ligand $CNAr^{Dipp2}$ (Ar^{Dipp2} = 2,6-(2,6-(i-$Pr)_2C_6H_3)_2C_6H_3$) and its less sterically encumbering derivative $CNAr^{Mes2}$ (Ar^{Mes2} = 2,6-(2,4,6-$Me_3C_6H_2)_2C_6H_3$) (see Chart 1).[26,28,35] In addition, we probed the ability of these ligands to bind technetium fragments in multiple oxidation states, such that stability profiles of metal−ligand binding could be gauged across multiple Tc redox states. These studies are intended to serve as the framework for uncovering a new generation of organometallic Tc cores with the required stability for nuclear-medical labeling experiments.

■ RESULTS AND DISCUSSION

$[Tc^I(NO)Cl_2(PPh_3)_2(MeCN)]$, $(NBu_4)[Tc^I{}_2(CO)_6Cl_3]$, $[Tc^{III}Cl_3(PMe_2Ph)_3]$, $[Tc^V(NPh)Cl_3(PPh_3)_2]$, and (NBu_4)-$[Tc^{VI}NX_4]$ (X = Cl, Br) have been used for ligation reactions with $CNAr^{Dipp2}$. All reactions were done in CH_2Cl_2, MeCN, or toluene without special protection against air or moisture. A summary of the obtained products is given in Scheme 1. It should be mentioned that related reactions with (NBu_4)-$[Tc^VOCl_4]$ did not yield defined technetium-containing products. Instead, an oxygen transfer to the ligand and the formation of the corresponding isocyanate was observed.

The dimeric technetium(I) complex (NBu_4)-$[Tc_2(CO)_6Cl_3]$[36,37] has been found to be a suitable substitute for $(NEt_4)_2[Tc(CO)_3Cl_3]$ as a precursor for the synthesis of tricarbonyltechnetium(I) complexes.[38] It reacts cleanly in THF with 2 equiv of $CNAr^{Dipp2}$ at room temperature to form *trans,mer*-$[Tc(CO)_3Cl(CNAr^{Dipp2})_2]$. The pale yellow solid is the sole product of the reaction. We found no evidence for the formation of ligand-exchange intermediates such as the assumed “kinetic” product *cis,fac*-$[Tc(CO)_3Cl(CNAr^{Dipp2})_2]$ or the formation of solvent-coordinated species. This is surprising and is in contrast to the behavior of analogous rhenium complexes, where under mild conditions *cis,fac*-$[Re(CO)_3Cl$-$(CNAr^{Dipp2})_2]$ can be isolated. However, this compound also isomerizes to the corresponding *trans,mer* isomer upon heating in boiling toluene.[39] The isomerization of the facially coordinated carbonyl ligands in the starting material into a meridional arrangement has been observed before also for manganese, molybdenum, and tungsten complexes[28−30] but is without precedent for technetium. The use of 3 equiv of $CNAr^{Dipp2}$ did not yield products with more than two isocyanide ligands.

trans,mer-$[Tc(CO)_3Cl(CNAr^{Dipp2})_2]$ is fairly soluble in nonpolar organic solvents. A striking feature of the product is the meridional arrangement of the carbonyl ligands, which has been first concluded from the IR spectrum of the compound and was finally confirmed by an X-ray structural analysis (Figure 1a). The few Tc(I) complexes with a meridional CO arrangement contain two axial PPh_3 ligands and are formed by reductive carbonylation of high-valent technetium compounds.[40,41] Possible reasons for the preference of the isomer with two relatively strong σ donors in positions *trans* to each other have been discussed previously for the molybdenum compounds.

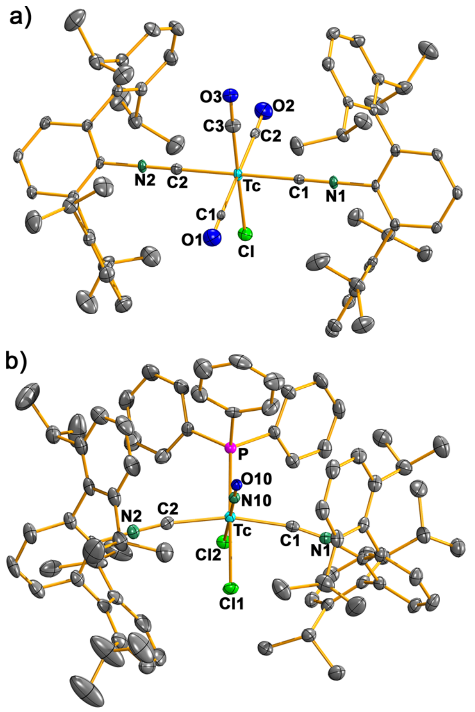


Figure 1. Molecular structures of the technetium(I) complexes (a) *trans,mer*-[Tc(CO)$_3$Cl(CNAr$^{\mathrm{Dipp2}}$)$_2$] and (b) *trans*-[Tc(NO)-Cl$_2$(PPh$_3$)(CNAr$^{\mathrm{Dipp2}}$)$_2$].

The hypothesis that the steric stress due to the bulky CNAr$^{\mathrm{Dipp2}}$ ligands is decisive[28] should also apply for the present technetium compound. It should be noted that in the two other structurally characterized tricarbonyl/isocyanide complexes of technetium, [Tc(CO)$_3$Cl(TBI)$_2$] and [Tc(CO)$_3$(TBI)]$^+$ (TBI = *tert*-butyl isocyanide), the expected facial coordination of the carbonyl ligands is established.[42,43]

Another structurally similar technetium(I) complex is formed from the reaction between [Tc(NO)Cl$_2$(PPh$_3$)$_2$(NCMe)] and CNAr$^{\mathrm{Dipp2}}$. The yellow *trans*-[Tc(NO)Cl$_2$(PPh$_3$)(CNAr$^{\mathrm{Dipp2}}$)$_2$] is extremely soluble in almost all nonpolar solvents, and single crystals of the compound for X-ray diffraction could only be obtained from *n*-hexane. An ellipsoid representation of the molecule is shown in Figure 1b. The axis containing the two isocyanide ligands is slightly bent (angle C1−Tc1−C2: 165.97(9)°) as a consequence of a *cis*-coordinated bulky PPh$_3$ ligand. The nitrosyl ligand is linearly coordinated and should thus be formally regarded as NO$^+$. The observed ν(NO) frequency of 1750 cm^{-1} reflects a considerable degree of back-donation to this ligand, which is typical for the d^6 configuration of Tc(I).

The ^{99}Tc NMR signals of the diamagnetic complexes appear at −1713 ppm (*trans,mer*-(Tc(CO)$_3$Cl(CNAr$^{\mathrm{Dipp2}}$)$_2$]) and −311 ppm ([Tc(NO)Cl$_2$(PPh$_3$)(CNAr$^{\mathrm{Dipp2}}$)$_2$]. This is the spectral range in which the signals of other tricarbonyltechnetium(I) and nitrosyltechnetium(I) complexes also appear.[28,42−45] However, particularly in the case of [Tc(NO)Cl$_2$(PPh$_3$)(CNAr$^{\mathrm{Dipp2}}$)$_2$], it is striking that the position within the entire range of Tc$^{\mathrm{I}}$(NO) complexes, which spans from +2000 to −1800 ppm, is close to that of nitrosyl complexes with coligands having no or only weak π-acceptor properties such as halides, H$_2$O, and PPh$_3$.[45] This is consistent with the CNAr$^{\mathrm{Dipp2}}$ ligands functioning as predominantly σ donors when other strongly π acidic ligands are present and has been observed previously in a series of mixed isocyanide/carbonyl cobalt complexes.[27] The isocyanide ν(CN) stretch for [Tc(NO)Cl$_2$(PPh$_3$)(CNAr$^{\mathrm{Dipp2}}$)$_2$] (2170 cm^{-1}) further supports this view, as it is considerably higher in energy that that of free CNAr$^{\mathrm{Dipp2}}$ (2124 cm^{-1}).

The signals of the asymmetric complexes are broad with half-line widths of approximately 5000 Hz due to the high nuclear spin of $I = 9/2$ and a large quadrupole moment of ^{99}Tc. Scalar couplings between the quadrupole moment of ^{99}Tc and the ^{31}P nucleus of the PPh$_3$ ligands are also believed to be responsible for the extreme line broadening of the ^{31}P NMR signal, which makes it practically invisible. Similar findings have been reported for a number of other diamagnetic technetium complexes.[40,46]

The ligand exchange of technetium compounds with CNAr$^{\mathrm{Dipp2}}$ is not restricted to starting materials having Tc in low formal oxidation states. The reaction of [TcCl$_3$(PMe$_2$Ph)$_3$] with an excess of CNAr$^{\mathrm{Dipp2}}$ results in the formation of [TcCl$_3$(PMe$_2$Ph)$_2$(CNAr$^{\mathrm{Dipp2}}$)] as the sole product. The formation of complexes with more than one CNAr$^{\mathrm{Dipp2}}$ ligand was not observed. This is unlike the situation with TBI, where during similar reactions with the same precursor up to five isocyanide ligands could be introduced.[47] [TcCl$_3$(PMe$_2$Ph)$_2$(CNAr$^{\mathrm{Dipp2}}$)] is an orange-red, crystalline solid, which is readily soluble in CH$_2$Cl$_2$, CHCl$_3$, and alcohols. The molecular structure of the complex is shown in Figure 2.

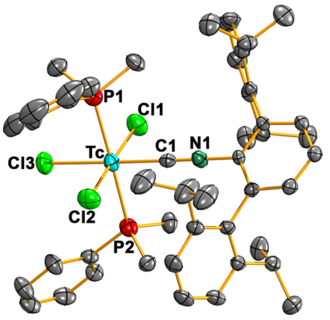


Figure 2. Molecular structure of [TcCl$_3$(PMe$_2$Ph)$_2$(CNAr$^{\mathrm{Dipp2}}$)].

The Tc−C bond of 2.034(5) Å is shorter than those in the technetium(I) complexes described above, which can mainly be attributed to the fact that the isocyanide is here bonded in a position *trans* to Cl$^-$ and not to another CNAr$^{\mathrm{Dipp2}}$ ligand.

As mentioned above, reactions of (NBu$_4$)[TcOCl$_4$] with the *m*-terphenyl ligands of this study were not successful and the formation of the corresponding isocyanates was observed. Nevertheless, technetium(V) complexes could be isolated with phenylimido and nitrido cores. A reaction of the sparingly soluble [Tc(NPh)Cl$_3$(PPh$_3$)$_2$] with CNAr$^{\mathrm{Dipp2}}$ in a CHCl$_3$/toluene mixture resulted in a rapid dissolution of the starting material and the formation of a green solution, from which green crystals of *trans*-[Tc(NPh)Cl$_3$(CNAr$^{\mathrm{Dipp2}}$)] were isolated. A subsequent reaction with Me$_3$SiBr gave the corresponding bromido analogue *trans*-[Tc(NPh)Br$_3$(CNAr$^{\mathrm{Dipp2}}$)]. The molecular structure of the chlorido complex is shown in Figure 3a. Since the structure of the bromido derivative is virtually identical, no extra figure is given here, but an ellipsoid representation of the molecule can be found in the Supporting Information.

Another high-valent technetium complex was obtained from the reaction of CNAr$^{\mathrm{Dipp2}}$ with (NBu$_4$)[TcNCl$_4$]. The technetium(VI) starting material was reduced, and the air-

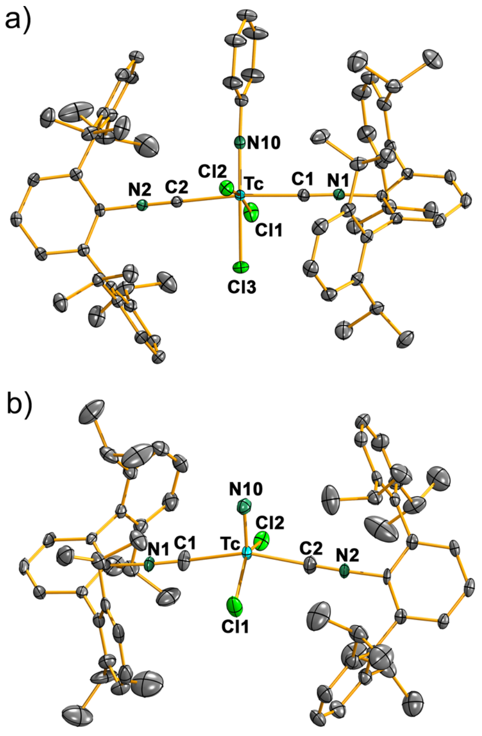
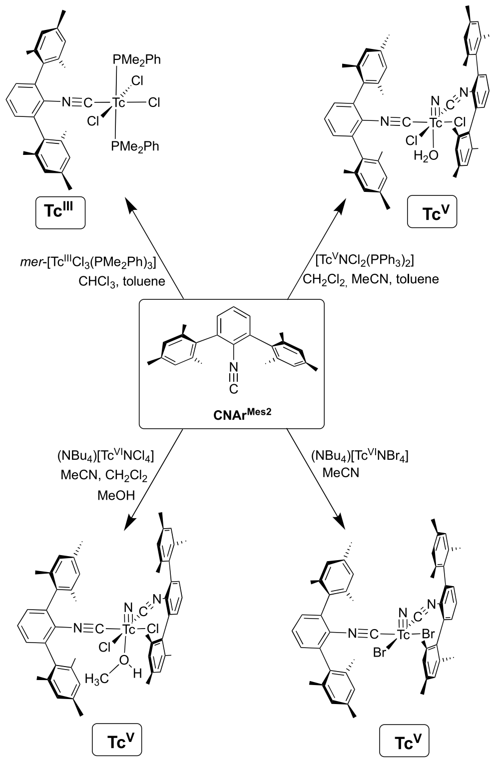


Figure 3. Molecular structures of the technetium(V) complexes (a) $[Tc(NPh)Cl_3(CNAr^{Dipp2})_2]$ and (b) $[TcNCl_2(CNAr^{Dipp2})_2]$.

Scheme 2. Reactions Performed with $CNAr^{Mes2}$



stable technetium(V) nitrido compound *trans*-$[TcNCl_2(CNAr^{Dipp2})_2]$ precipitated as an orange-red crystalline solid. The formation of technetium(V) complexes starting from $[TcNX_4]^-$ (X = Cl, Br) precursors is common and has been observed with many ligand systems. The few known organotechnetium(V) nitrides, however, have been prepared by ligand-exchange procedures starting from $[TcNCl_2(PPh_3)_2]$.[48,49] Similar to the analogous compounds $[TcNCl_2(PPh_3)_2]$ and $[TcN(Ph)_2(PPh_3)_2]$,[49] the coordination environment of the five-coordinate technetium atom is best described as a trigonal bipyramid with the two bulky $CNAr^{Dipp2}$ ligands in axial positions. The central $\{TcNCl_2\}$ core is disordered over three positions. Figure 3b shows an ellipsoid representation of the main component.

Since the previously discussed nitrido and phenylimido complexes with the sterically encumbered $CNAr^{Dipp2}$ ligand are the first stable isocyanide complexes of technetium in the oxidation state +5, we were interested to learn more about the protective role of the bulky isocyanides. Thus, we also undertook some reactions with the sterically less encumbered ligand $CNAr^{Mes2}$. We restricted these preliminary experiments to reactions with nitrido complexes in order to see if the high oxidation state of the metal can also be stabilized by $CNAr^{Mes2}$ and if different isomers are formed as a function of the steric load.

An additional experiment with $[TcCl_3(PMe_2Ph)_3]$ should answer the question if the use of the less bulky ligand allows the coordination of two or more ligands at the Tc(III) center. A summary of the reactions and their products is shown in Scheme 2.

Irrespective of the starting materials ($[TcNCl_2(PPh_3)_2]$ or $(NBu_4)[TcNX_4]$ (X = Cl, Br)), nitridotechnetium(V) complexes with two $CNAr^{Mes2}$ ligands in a *cis* arrangement were formed. The occupation of the (frequently vacant) sixth coordination position in nitridotechnetium complexes during the crystallization procedure by solvent molecules such as alcohols and water is not unusual and has been observed for a number of examples before.[50,51] Figure 4a illustrates the molecular structure of *cis*-$[TcNCl_2(CNAr^{Mes2})_2(H_2O)]$, and the structure of the corresponding MeOH derivative is given in the Supporting Information. Expectedly, the Tc−C bonds in the *cis* isomers (2.039−2.066 Å) are somewhat shorter than in *trans*-$[TcNCl_2(CNAr^{Dipp2})_2]$ (2.098−2.116 Å), which is in line with the situation in the corresponding molybdenum and manganese complexes and can be attributed to the higher structural *trans* influence of the *m*-terphenyl isocyanides in comparison to halides.

The isolation of $[TcCl_3(PMe_2Ph)_2(CNAr^{Mes2})]$ as the sole product of the reaction of $[TcCl_3(PMe_2Ph)_3]$ with $CNAr^{Mes2}$ supports our hypothesis that the coordination of only one $CNAr^{Dipp2}$ ligand in $[TcCl_3(PMe_2Ph)_2(CNAr^{Dipp2})]$ is not caused by steric factors. Attempted reactions with a 3-fold excess of both isocyanides did not result in the exchange of more than one phosphine ligand.

A remarkable spectroscopic feature is given with the positions of the ν(CN) IR frequencies. They are summarized in Table 1 together with some other selected IR bands. It is evident that only in the case of the technetium(III) complexes can a considerable degree of back-donation into isocyanide orbitals be concluded from the IR data. For the electron-poor technetium(V) complexes, the binding of the ligands as effective σ donors without considerable back-donation is not unexpected. In the considered electron-rich technetium(I) complexes, however, an efficient back-donation is expected preferably to their carbonyl and nitrosyl ligands, which are powerful π acceptors. For a more detailed estimation of the bonding situation inside the technetium compounds of the present study, it would be interesting to have *m*-terphenyl isocyanide complexes of

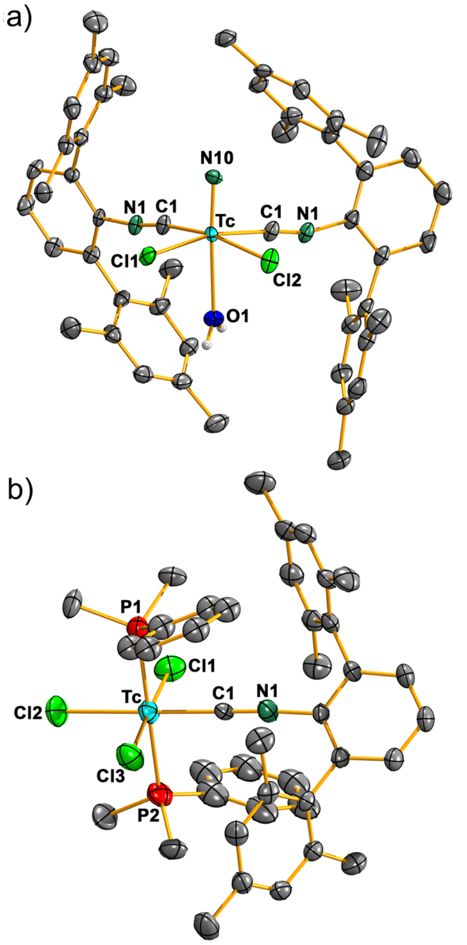


Figure 4. Molecular structures of (a) *cis*-$[TcNCl_2(CNAr^{Mes2})_2(H_2O)]$ and (b) $[TcCl_3(PMe_2Ph)_2(CNAr^{Mes2})]$.

Table 1. Selected IR Frequencies

	ν(CN)	others
$CNAr^{Dipp2}$	2124	
$[Tc(CO)_3Cl(CNAr^{Dipp2})_2]$	2152	CO: 2039, 1989, 1938
$[Tc(NO)Cl_2(PPh_3)(CNAr^{Dipp2})_2]$	2170	NO: 1750
$[TcCl_3(PMe_2Ph)_2(CNAr^{Dipp2})]$	2089	
$[TcNCl_2(CNAr^{Dipp2})_2]$	2174	TcN: 1047
$[TcNBr_2(CNAr^{Dipp2})_2]$	2176	TcN: 982
$[Tc(NPh)Cl_3(CNAr^{Dipp2})_2]$	2187	
$[Tc(NPh)Br_3(CNAr^{Dipp2})_2]$	2182	
$CNAr^{Mes2}$	2120	
$[TcCl_3(PMe_2Ph)_2(CNAr^{Mes2})]$	2108	
$[TcNCl_2(CNAr^{Mes2})_2(H_2O)]$	2179	TcN: 1073
$[TcNCl_2(CNAr^{Mes2})_2(MeOH)]$	2179	TcN: 1073
$[TcNBr_2(CNAr^{Mes2})_2]$	2174	TcN: 1036

technetium(I) available without additional π-acceptor ligands: e.g. such as a comparison with the hexakis complex $[Tc(sestamibi)_6]^+$ shown in Chart 1.

■ CONCLUSIONS

Sterically encumbered *m*-terphenyl isocyanides stabilize technetium complexes having various cores and the metal in different oxidation states (+1 to +5). The products are air-stable, and particularly the compounds with two *trans*-coordinated $CNAr^{Dipp2}$ ligands possess highly shielded metal centers. The effectiveness of this shielding makes them interesting for nuclear medical consideration: e.g., as a potential radioactive tracer for the bioconjugation approach. Given that competitive ligand-exchange reactions with blood components are hindered by the steric protection, the compounds are suitable chemical foundations for coupling reactions with peptides or other biologically active molecules. For this purpose, the replacement of the Cl^- ligand in *trans,mer*-$[Tc(CO)_3Cl(CNAr^{Dipp2})_2]$ by e.g. long-chained, ω-substituted thiols or the use of a phenylimido complex with an appropriate substitution (e.g., a carboxylic group) in the 4-position might be possible approaches.

■ EXPERIMENTAL SECTION

Materials. All chemicals used were reagent grade and were used without further purification. ^{99}Tc was purchased as solid ammonium pertechnetate from Oak Ridge National Laboratory (ORNL). The salt was purified by recrystallization from aqueous solutions. For this, the gray-black crystalline solid obtained from ORNL was dissolved in a minimum amount of warm water (60 °C) and filtered through a fine-porosity glass frit, leaving behind a very small amount of a black solid ($TcO_2 \cdot nH_2O$). The filtrate was brought to dryness by evaporation of the water, giving large colorless crystals of pure $(NH_4)TcO_4$.[52] $CNAr^{Dipp2}$,[28] $CNAr^{Mes2}$,[35] $[Tc^I(NO)Cl_2(PPh_3)_2(MeCN)]$,[53] $[Tc^{III}Cl_3(PMe_2Ph)_3]$,[54] $[Tc^VNCl_2(PPh_3)_2]$,[55] $(NBu_4)[Tc^VOCl_4]$,[56] and $(NBu_4)[Tc^{VI}NCl_4]$[57] were prepared by literature procedures.

Physical Measurements. IR spectra (KBr) were measured with a Shimadzu FTIR Affinity-1 spectrometer between 400 and 4000 cm^{-1}. NMR spectra were recorded at 25 °C on JEOL 400 MHz spectrometers. Chemical shifts (δ) are given relative to the signals of external standards (tetramethylsilane (^1H), 85% phosphoric acid (^{31}P), and NH_4TcO_4 in D_2O (^{99}Tc)).

The technetium contents of the samples were measured by a HIDEX 300 SL liquid scintillation counter. An aliquot of three probes per sample with different concentrations was added to 10 mL of a scintillation cocktail (Rotiszint ecoplus, Carl Roth), and the net count rates were measured over 1024 channels with a counting time of 60 s. An average value was calculated for each sample. The appearance of quenching effects cannot be excluded completely during the measurement of colored compounds and may result in some minor deviations from the calculated values.

Radiation Precautions. ^{99}Tc is a long-lived weak β^- emitter (E_{max} = 0.292 MeV). Normal glassware provides adequate protection against the weak β 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.

X-ray Crystallography. The intensities for the X-ray determinations were collected on a Bruker D8 Venture instrument or an STOE IPDS 2T instrument with Mo Kα radiation. The space groups were determined by the detection of systematic absences. Absorption corrections were carried out with SADABS or X-RED 32.[58,59] Structure solution and refinement were performed with the SHELX program package.[60,61] Hydrogen atoms were placed at calculated positions and treated with the "riding model" option of SHELXL. The representation of molecular structures was done using the program DIAMOND 4.2.2.[62]

Additional information on the structure determinations is contained in the Supporting Information and has been deposited with the Cambridge Crystallographic Data Centre.

Synthesis of the Complexes. *trans,mer*-$[Tc(CO)_3Cl(CNAr^{Dipp2})_2]$. $(NBu_4)[Tc_2(CO)_6Cl_3]$ (34 mg, 0.05 mmol) and $CNAr^{Dipp2}$ (84 mg, 0.2 mmol) were dissolved in 5 mL of THF and stirred overnight at room temperature. During this time, a pale yellow solid was formed, which was filtered off and dried. Concentration of the solvent to approximately 0.5 mL and addition of methanol (3 mL) resulted in the formation of more product. Yield: 76 mg (72%). Anal. Calcd for $C_{65}H_{74}ClN_2O_3Tc$: Tc, 9.3. Found: Tc, 8.6. IR (cm^{-1}): 2961 (w), 2916 (w), 2857 (w), ν(CN) 2152 (s), ν(CO) 2039 (s), ν(CO) 1989 (s), ν(CO) 1938 (s), 1612 (w), 1458 (w), 1377 (w), 1273 (w), 893 (w), 852 (m), 785 (w), 607 (w), 582 (w). ^{1}H NMR (CD_2Cl_2, ppm): 7.48−7.22 (m, 9H), 2.45 (hept, *J* = 6.8 Hz, 4H), 1.09 (dd, *J* = 6.8 Hz, 24H). ^{99}Tc NMR (CD_2Cl_2, ppm): −1713.

[Tc(NO)Cl$_2$(PPh$_3$)(CNAr^{Dipp2})$_2$]. CNAr^{Dipp2} (84 mg, 0.2 mmol) was added to a stirred suspension of [Tc(NO)Cl_2(PPh$_3$)$_2$(CH$_3$CN)] (77 mg, 0.1 mmol) in 3 mL of toluene. The mixture was heated under reflux for 10 min. During this time, the sparingly soluble starting complex dissolved completely, and the mixture turned yellow. The solvent was removed, and the oily yellow residue was redissolved in warm *n*-hexane (3 mL). Upon concentration of this solution, some colorless material (OPPh$_3$) deposited and was removed by filtration. Further slow concentration of the hexane solution gave yellow plates of the product suitable for X-ray diffraction. Yield: 95 mg (73%). Anal. Calcd for $C_{80}H_{89}Cl_2N_3OPTc$: Tc, 7.5. Found: Tc, 6.5%. IR (cm^{-1}): 2960 (m), ν(CN) 2170 (s), ν(NO) 1750 (s), 1520 (w), 1320 (w), 1260 (s), 1190 (m), 1080 (s), 1010 (s), 796 (s), 696 (s). ^{1}H NMR (CD_2Cl_2, ppm): 7.49−7.47 (m, 2H), 7.21−7.37 (m, 15H) 7.08−7.18 (m, 12H), 6.94−6.98 (m, 4H), 2.42−2.55 (m, 8H), 0.95−1.16 (m, 48H). ^{99}Tc NMR (CD_2Cl_2, ppm): −316.

[TcCl$_3$(PMe$_2$Ph)$_2$(CNAr^{Dipp2})]. *mer*-[TcCl$_3$(PPhMe$_2$)$_3$] (62 mg, 0.1 mmol) was dissolved in 3 mL of CHCl$_3$, and CNAr^{Dipp2} (85 mg, 0.2 mmol) was added dissolved in 3 mL of toluene. The orange-red mixture was heated under reflux for 1 h. The solution was then filtered, and the solvent was reduced in volume. Red needles suitable for X-ray diffraction were obtained upon slow evaporation of the solvent. Yield: 65 mg (72%). Anal. Calcd for $C_{47}H_{59}Cl_3NP_2Tc$: Tc, 10.9. Found: Tc, 10.1. IR (cm^{-1}): 2967 (s), 2372 (m) ν(CN) 2089 (s), 1744 (w), 1514 (w), 1460 (m), 1092 (m), 1049 (s), 908 (s), 748 (s), 692 (m).

[Tc(NPh)Cl$_3$(CNAr^{Dipp2})$_2$]. [Tc(NPh)Cl$_3$(PPh$_3$)$_2$] (41 mg, 0.05 mmol) was suspended in 3 mL of toluene, and CNAr^{Dipp2} (42 mg, 0.1 mmol) was added. The mixture was heated under reflux for 1 h, giving a clear solution. Single crystals suitable for X-ray diffraction were obtained by slow evaporation of the reaction mixture. Yield: 91 mg (80%). Anal. Calcd for $C_{68}H_{79}Cl_3N_3Tc$: Tc, 8.7. Found: Tc, 7.9. IR (cm^{-1}): 2959 (s), 2922 (m), ν(CN) 2187 (s), 1462 (m), 799 (w), 754 (m). ^{1}H NMR (CD_2Cl_2, ppm): 7.93−7.83 (m, 1H), 7.53 (t, *J* = 7.6 Hz, 2H), 7.46−7.39 (m, 2H), 7.31−7.20 (m, 6H), 7.15−7.07 (m, 4H), 6.99 (d, *J* = 7.7 Hz, 8H), 2.39 (hept, *J* = 6.8 Hz, 8H), 1.05 (d, *J* = 6.8 Hz, 24H), 1.02 (d, *J* = 6.8 Hz, 24H).

[Tc(NPh)Br$_3$(CNAr^{Dipp2})$_2$]. [Tc(NPh)Cl$_3$(CNAr^{Dipp2})$_2$] (40.0 mg, 0.04 mmol) was suspended in toluene (2 mL), 200 μL of trimethylsilyl bromide was added, and the mixture was heated under reflux for 30 min. The reaction mixture turned orange-red. Single crystals suitable for X-ray diffraction were obtained by slow evaporation of the reaction mixture. They were washed with a small amount of hexane. Yield: 41 mg (85%). Anal. Calcd for $C_{75}H_{87}Br_3N_3Tc$: Tc, 7.2. Found: Tc, 7.4. IR (cm^{-1}): 2958 (s), 2885 (w), 2181 (s), 1576 (w), 1458 (m), 1361 (w), 1056 (w), 794 (s), 766 (m), 735 (s), 669 (s). ^{1}H NMR (CD_2Cl_2, ppm): 7.60−7.42 (m, 5H), 7.29−6.93 (m, 18H), 2.46−2.35 (m, 8H), 1.14−0.96 (m, 48H).

[TcNCl$_2$(CNAr^{Dipp2})$_2$]. CNAr^{Dipp2} (85 mg, 0.2 mmol) dissolved in 1 mL of CH_2Cl_2 was added to a stirred solution of (NBu$_4$)[TcNCl$_4$] (50 mg, 0.1 mmol) in MeCN (2 mL). A few drops of MeOH were added, and the red solution became dark brown. After the addition of 2 mL of toluene, the reaction mixture was kept overnight for slow evaporation. The deposited red crystals were filtered off and washed with a small amount of toluene. Yield: 87 mg (85%). Anal. Calcd for $C_{62}H_{74}Cl_2N_3Tc$: Tc, 9.6. Found: Tc, 10.3. IR (cm^{-1}): 2965 (m), 2874 (m), ν(CN) 2174 (s), 1460 (s), 1381 (w), 1047 (s), 881 (m), 746 (m), 758 (m). ^{1}H NMR (CD_2Cl_2, ppm): 7.60 (m, 2H), 7.39 (m, 4H), 7.33 (d, *J* = 7.7 Hz, 4H), 7.22 (m, 8H), 2.44 (qq, *J* = 6.8 Hz, 8H), 1.12 (d, *J* = 6.9 Hz, 24H), 1.09 (d, *J* = 6.8 Hz, 24H).

[TcNBr$_2$(CNAr^{Dipp2})$_2$]. CNAr^{Dipp2} (84 mg, 0.2 mmol) was dissolved in 1 mL of CH_2Cl_2 and added to a stirred solution of (NBu$_4$)[TcNBr$_4$] (34 mg, 0.05 mmol) in 2 mL of MeCN. After the addition of a few drops of MeOH, a red precipitate was formed within 5 min. The solid was filtered off, washed with diethyl ether, and recrystallized from CH_2Cl_2/diethyl ether. Yield: 89 mg (80%). Anal. Calcd for $C_{62}H_{74}Br_2N_3Tc$: Tc, 8.8. Found: Tc, 9.1. IR (cm^{-1}): 2960 (w), ν(CN) 2176 (s), 1461 (m), 1234 (s), 982 (m), 796 (m), 752 (m). ^{1}H NMR (CD_2Cl_2, ppm): 7.60 (m, 2H), 7.41−7.31 (m, 8H), 7.20 (m, 8H), 2.45 (qq, *J* = 6.8 Hz, 8H), 1.12 (d, *J* = 6.9 Hz, 24H), 1.08 (d, *J* = 6.8 Hz, 24H).

[TcCl$_3$(PMe$_2$Ph)$_2$(CNAr^{Mes2})$_2$]. [TcCl$_3$(PMe$_2$Ph)$_3$] (31 mg, 0.05 mmol) was dissolved in 3 mL of CHCl$_3$, and CNAr^{Mes2} (34 mg, 0.1 mmol) was added in 3 mL of toluene. The orange-red mixture was heated under reflux for 1 h. The solution was then filtered, and the solvent was removed under vacuum. Red needles suitable for X-ray diffraction were obtained upon slow evaporation of an ethanol/hexane solution. Yield: 31 mg (75%). Anal. Calcd for $C_{41}H_{47}Cl_3NP_2Tc$: Tc, 12.1. Found: Tc, 12.5. IR (cm^{-1}): 2916 (m), ν(CN) 2108 (s), 1435 (m), 1406 (w), 1261 (s), 901 (m), 745 (m), 691 (m).

[TcNCl$_2$(CNAr^{Mes2})$_2$(MeOH)]. CNAr^{Mes2} (68 mg, 0.2 mmol) was dissolved in 1 mL of CH_2Cl_2 and added to a stirred solution of (NBu$_4$)[TcNCl$_4$] (50 mg, 0.1 mmol) in 2 mL of MeCN. A few drops of MeOH were added, and the solution was heated under reflux for 30 min. The solvents were removed under vacuum, and the remaining solid was dissolved in a small quantity of a CH_2Cl_2/MeOH mixture (10/1). Overlayering with *n*-hexane and slow diffusion of the solvents gave orange-red crystals. Yield: 70 mg (80%). IR (cm^{-1}): 2918 (w), 2203 (m), ν(CN) 2179 (s), 1612 (w), 1457 (s), 1380 (w), 1186 (w), 1073 (s), 854 (m), 809 (m), 755 (s). ^{1}H NMR (CD_2Cl_2, ppm): 7.61 (m, 2H), 7.30 (m, 4H), 6.91 (m, 8H), 2.28 (s, 12H), 2.03 (d, *J* = 2.8 Hz, 24H).

[TcNCl$_2$(CNAr^{Mes2})$_2$(H$_2$O)]. CNAr^{Mes2} (68 mg, 0.2 mmol) dissolved in 1 mL of CH_2Cl_2 was added to a stirred suspension of [TcNCl$_2$(PPh$_3$)$_2$] (71 mg, 0.1 mmol) in 2 mL of MeCN. Toluene (3 mL) was added, and the mixture was heated under reflux for 90 min. Orange-red crystals deposited during slow evaporation of the reaction mixture. They were filtered off and washed with a small amount of cold toluene. Yield: 58 mg (65%). Anal. Calcd for $C_{50}H_{52}Cl_2N_3OTc$: Tc, 11.2. Found: Tc, 10.1. IR (cm^{-1}): 2918 (w), 2203 (m), ν(CN) 2179 (s), 1612 (w),1457 (s), 1380 (w), 1186 (w), 1073 (s), 854 (m), 809 (m), 755 (s). ^{1}H NMR (CD_2Cl_2, ppm): 7.61 (m, 2H), 7.30 (m, 4H), 6.91 (m, 8H), 2.28 (s, 12H), 2.03 (d, *J* = 2.8 Hz, 24H).

[TcNBr$_2$(CNAr^{Mes2})$_2$]. CNAr^{Mes2} (68 mg, 0.2 mmol) was dissolved in 2 mL of CH_2Cl_2 and added to a stirred solution of (NBu$_4$)[TcNBr$_4$] (34 mg, 0.05 mmol) in 2 mL of MeCN. A few drops of MeOH were added, and the solution was stirred for 30 min at room temperature. After the addition of 3 mL of toluene and slow evaporation of the solvent, a solid was obtained. It was filtered off and washed with a small amount of cold toluene. Yield: 70 mg (75%). Anal. Calcd for $C_{50}H_{50}Br_2N_3Tc$: Tc, 10.4. Found: Tc, 9.5. IR (cm^{-1}): 3422 (br), 2916 (m), 2865 (w), ν(CN) 2174 (s), 1456 (m), 1036 (w), 854 (2), 752 (w). ^{1}H NMR (CD_2Cl_2, ppm): 7.61 (m, 2H), 7.30 (m, 4H), 6.95−6.86 (m, 8H), 2.28 (d, *J* = 6.1 Hz, 12H), 2.03 (d, *J* = 6.3 Hz, 24H).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.0c00238.

Crystallographic data, bond lengths, angles, and ellipsoid plots and spectroscopic data (PDF)

Accession Codes

CCDC 1989548−1989556 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

■ AUTHOR INFORMATION

Corresponding Authors

Joshua S. Figueroa − *Department of Chemistry and Biochemistry, University of California, San Diego, La Jolla, California 92093,* United States; orcid.org/0000-0003-2099-5984; Email: jsfig@ucsd.edu

Ulrich Abram – *Freie Universität Berlin, Institute of Chemistry and Biochemistry, D-14195 Berlin, Germany;* orcid.org/0000-0002-1747-7927; Email: ulrich.abram@fu-berlin.de

Authors

Guilhem Claude – *Freie Universität Berlin, Institute of Chemistry and Biochemistry, D-14195 Berlin, Germany*

Federico Salsi – *Freie Universität Berlin, Institute of Chemistry and Biochemistry, D-14195 Berlin, Germany*

Adelheid Hagenbach – *Freie Universität Berlin, Institute of Chemistry and Biochemistry, D-14195 Berlin, Germany*

Milan Gembicky – *Department of Chemistry and Biochemistry, University of California, San Diego, La Jolla, California 92093, United States*

Michael Neville – *Department of Chemistry and Biochemistry, University of California, San Diego, La Jolla, California 92093, United States*

Chinglin Chan – *Department of Chemistry and Biochemistry, University of California, San Diego, La Jolla, California 92093, United States*

Complete contact information is available at:
https://pubs.acs.org/10.1021/acs.organomet.0c00238

Notes

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