

Tricarbonylrhenium(I) and -technetium(I) Complexes with Tris(1,2,3-triazolyl)phosphine Oxides

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Two potentially tripodal ligands, tris(1-phenyl-1*H*-1,2,3-triazol-4-yl)phosphine oxide (OP^(1,2,3Tz^{1-Ph})₃) and tris(1-benzyl-1*H*-1,2,3-triazol-4-yl)phosphine oxide (OP^(1,2,3Tz^{1-benz})₃), were used in reactions with [Re(CO)₅Br] and (NEt₄)₂[Tc(CO)₃Cl₃]. While the formation of rhenium complexes with bidentate and tridentate

coordinated phosphine oxides was observed, for technetium only cationic complexes with tripodal coordinated OP^(1,2,3Tz^{1-R})₃ ligands were isolated. The products have been characterized spectroscopically and by single crystal X-ray diffraction.

Introduction

Stable and kinetically inert tricarbonyl complexes of rhenium and technetium are of ongoing interest for the development of novel radiopharmaceuticals for diagnostics and therapy.^[1–9] The metastable nuclear isomer ^{99m}Tc is still the ‘workhorse’ in diagnostic nuclear medicine with some 40 million annual administrations worldwide,^[10] and rhenium possesses two β[–]-emitting isotopes suitable for therapy: ¹⁸⁶Re and ¹⁸⁸Re. For both elements, normal pressure syntheses have been developed for corresponding [M(CO)₃(H₂O)₃]⁺ (M = ^{99m}Tc, ¹⁸⁸Re) cations, which are perfect precursors for nuclear medical preparations.^[11,12] The stability of the formed complexes is mainly governed by the denticity of used ligands,^[13] which directed the focus of interest preferably to tridentate ligand systems.^[14–20] This includes pseudotripodal systems such as cyclopentadienyl ligands.^[21–26] But also scorpionate ligands with various backbones and donor atom constellations found attention in this context. This includes the classical tris(pyrazolyl)borates, tris(pyrazolyl)methanes and poly(mercaptoimidazolyl)borates,^[7,8,27–37] but also such with a central phosphorus atom.^[38]

One of the reason for the development of carbon- and phosphorus-centered ligand systems was the intention to

improve the stability of such ligands by the replacement of the hydrolytically less stable B–N bonds by more stable C–N or C–P bonds.^[38] In this context, also tris(1,2,3-triazolyl)phosphines and their oxides have been developed as ligands for transition metal ions and some of their complexes with platinum, copper, rhodium and tungsten have been described.^[39–41]

In the present study we describe syntheses and structures of tricarbonylrhenium(I) and -technetium(I) complexes with tris(1-phenyl-1*H*-1,2,3-triazol-4-yl)phosphine oxide, OP^(1,2,3Tz^{1-Ph})₃, and tris(1-benzyl-1*H*-1,2,3-triazol-4-yl)phosphine oxide, OP^(1,2,3Tz^{1-benz})₃ (Figure 1).

Results and Discussion

The tris(1,2,3-triazolyl)phosphine oxides of Figure 1 can readily be prepared in high yields by copper-catalyzed Huisgen cycloadditions between tris(ethylenyl)phosphine oxide and organic azides. The procedure has been developed by K. Lammertsma for the phenyl-substituted ligand,^[39] but works also with benzyl azide and gives OP^(1,2,3Tz^{1-benz})₃ in high purity and with a yield of 95 per cent.

Reactions of [Re(CO)₅Br] with OP^(1,2,3Tz^{1-Ph})₃ or OP^(1,2,3Tz^{1-benz})₃ in boiling CHCl₃ result in the replacement of two carbonyl ligands and the formation of [Re(CO)₃Br{OP^(1,2,3Tz^{1-R})₃}] complexes (Scheme 1). Remarkably, these reactions are not

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Supporting information for this article is available on the WWW
under <https://doi.org/10.1002/zaac.202100010>

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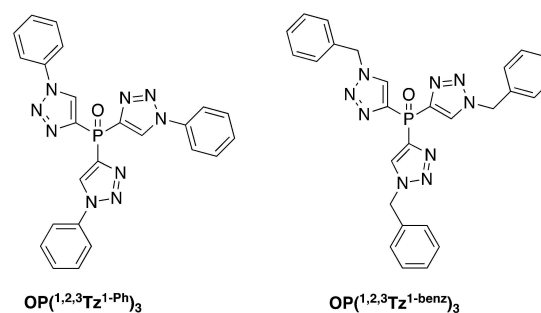
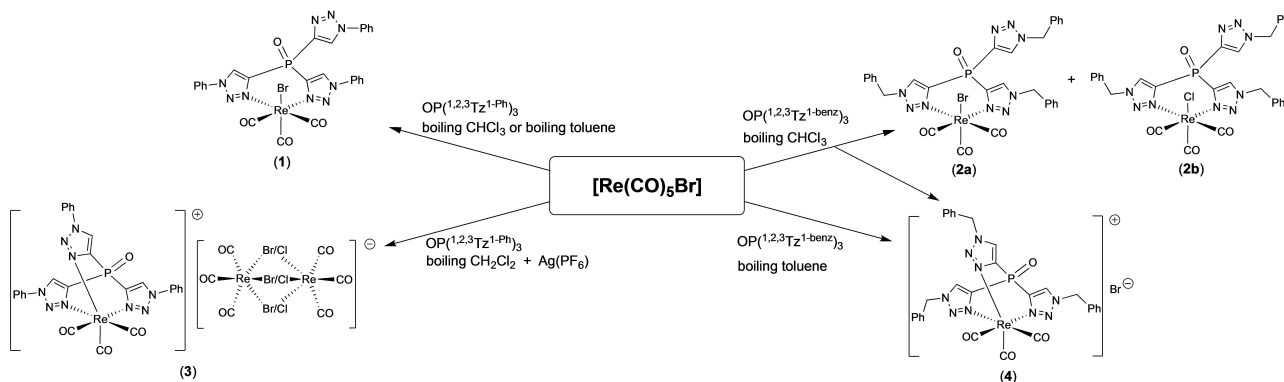


Figure 1. Tris(1,2,3-triazolyl)phosphine oxides used in the present study.



Scheme 1. Reactions performed starting from $[\text{Re}(\text{CO})_5\text{Br}]$ and their products.

straightforward and accompanied by a number of side-reactions, which lower the yields and result in the formation of a number of decomposition products. It should also be mentioned that the marginal modifications in the backbone of the ligands (phenyl vs. benzyl in a peripheral position) seem to have an unexpected influence on the course of the reactions. Finally, we succeeded in the isolation of pure $[\text{Re}(\text{CO})_3\text{Br}\{\kappa^2\text{N},\text{N}'\text{-OP}(1,2,3\text{Tz}^1\text{-Ph})_3\}]$ (1), while during the analogous reaction with $\text{OP}(1,2,3\text{Tz}^1\text{-benz})_3$ chloride abstraction from the solvent CHCl_3 and the formation of considerable amounts of the corresponding chlorido complex $[\text{Re}(\text{CO})_3\text{Cl}\{\kappa^2\text{N},\text{N}'\text{-OP}(1,2,3\text{Tz}^1\text{-benz})_3\}]$ (2b) was observed. This Br/Cl exchange was not an accidental effect of one single reaction mixture, but has been found to be systematic. Although NMR and IR spectroscopy give no safe evidence for the formation of a mixture of the very similar compounds $[\text{Re}(\text{CO})_3\text{Br}\{\kappa^2\text{N},\text{N}'\text{-OP}(1,2,3\text{Tz}^1\text{-benz})_3\}]$ (2a) and $[\text{Re}(\text{CO})_3\text{Cl}\{\kappa^2\text{N},\text{N}'\text{-OP}(1,2,3\text{Tz}^1\text{-benz})_3\}]$ (2b), the presence of considerable amounts of both compounds in the formed solid is proven by mass spectrometry, elemental analysis and X-ray diffraction. Figure 2 is a section of the (+)-ESI mass spectrum of the bulk product illustrating the molecular ion region of the two complexes. Clearly, the Na^+ and K^+ adducts of the chlorido and bromido complexes with the correct isotopic patterns can be identified.

An approximate Br:Cl ratio of 3:7 fits best the elemental analysis of the product as well as the single-crystal X-ray structure refinement of the single crystals obtained from the reaction product. Both complexes co-crystallize in a triclinic unit cell. Details about the structure determination and refinement are given in the Supporting Information. Individual bond lengths and angles of the $[\text{Re}(\text{CO})_3\text{X}\{\kappa^2\text{N},\text{N}'\text{-OP}(1,2,3\text{Tz}^1\text{-benz})_3\}]$ (2) ($\text{X}=\text{Cl}, \text{Br}$) complexes shall not be discussed here because of their origin from a mixed-crystal structure analysis. In general, the molecular structure is very similar to that of the analogous complex $[\text{Re}(\text{CO})_3\text{Br}\{\kappa^2\text{N},\text{N}'\text{-OP}(1,2,3\text{Tz}^1\text{-Ph})_3\}]$ (1), which is depicted in Figure 3a. Selected bond lengths and angles are summarized in Table 1.

The coordination sphere of rhenium in $[\text{Re}(\text{CO})_3\text{Br}\{\kappa^2\text{N},\text{N}'\text{-OP}(1,2,3\text{Tz}^1\text{-Ph})_3\}]$ (1) is an only slightly distorted octahedron. Some marginal deviations from the ideal 90° and 180° angles

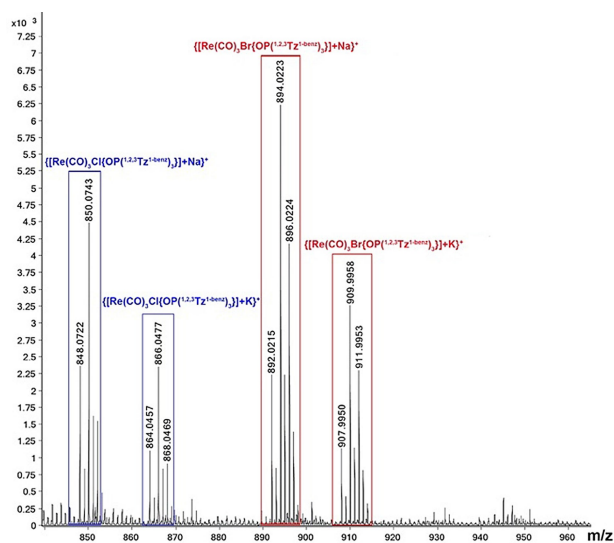


Figure 2. Molecular ion regions of the (+)-ESI mass spectra of the complexes $[\text{Re}(\text{CO})_3\text{Br}\{\kappa^2\text{N},\text{N}'\text{-OP}(1,2,3\text{Tz}^1\text{-benz})_3\}]$ (2a) and $[\text{Re}(\text{CO})_3\text{Cl}\{\kappa^2\text{N},\text{N}'\text{-OP}(1,2,3\text{Tz}^1\text{-benz})_3\}]$ (2b) detected in the bulk product of the reaction between $[\text{Re}(\text{CO})_5\text{Br}]$ and $\text{OP}(1,2,3\text{Tz}^1\text{-benz})_3$ in CHCl_3 .

are due to the chelate formation of the phosphine oxide. But obviously, the bidentate coordination of this ligands does not cause a considerably steric stress.

The ^{31}P NMR spectrum of the complex shows a single resonance at -8.2 ppm in CDCl_3 , which is only a slight shift compared to the uncoordinated ligand (-5.7 ppm).^[39] In the (+)-ESI mass spectrum of $[\text{Re}(\text{CO})_3\text{Br}\{\kappa^2\text{N},\text{N}'\text{-OP}(1,2,3\text{Tz}^1\text{-Ph})_3\}]$ (1), there is no evidence for a Br/Cl exchange as has been observed for the corresponding complex with $\text{OP}(1,2,3\text{Tz}^1\text{-benz})_3$. The molecular ion region of the spectrum shows one intense signal at $m/z=750.068$, which can clearly be assigned to the $[\text{M}-\text{Br}]^+$ ion. The non-symmetric coordination sphere of the rhenium atom in $[\text{Re}(\text{CO})_3\text{Br}\{\kappa^2\text{N},\text{N}'\text{-OP}(1,2,3\text{Tz}^1\text{-Ph})_3\}]$ (1) is well reflected by the appearance of three CO vibrations at 1898 , 1931 and 2031 cm^{-1} .

The formation of cationic $[\text{Re}(\text{CO})_3\{\kappa^3\text{N},\text{N}'\text{-OP}(1,2,3\text{Tz}^1\text{-R})_3\}]^+$ complexes can be achieved when more drastic reaction

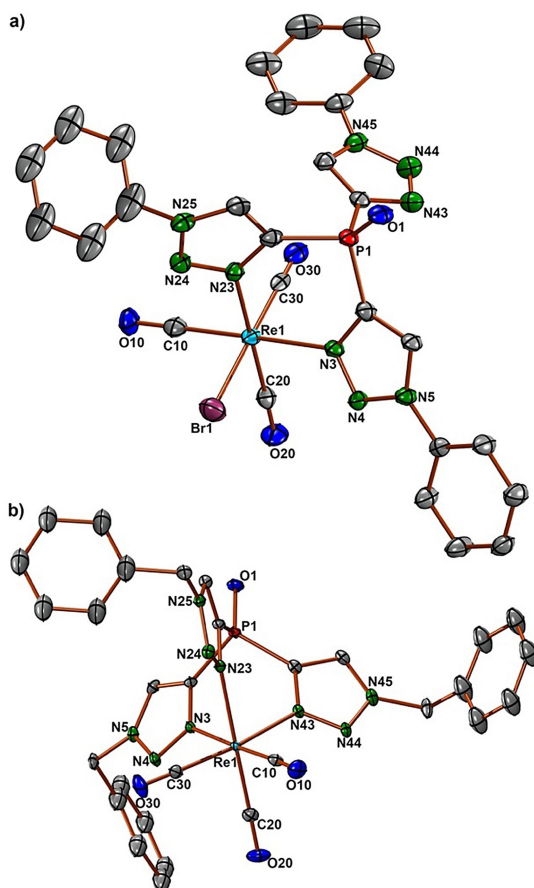


Figure 3. Ellipsoid representations of a) the molecular structure of $[\text{Re}(\text{CO})_3\text{Br}\{\kappa^2\text{N,N}'\text{-OP}(\text{1,2,3-Tz}^1\text{-Ph})_3\}]$ (1) and b) the cation of $[\text{Re}(\text{CO})_3\{\kappa^2\text{N,N}'\text{-OP}(\text{1,2,3-Tz}^1\text{-Ph})_3\}]\text{Br}$ (4). Thermal ellipsoids represent 50 per cent probability. Hydrogen atoms are omitted for clarity.

Table 1. Selected bond lengths (Å) and angles (°) in $[\text{Re}(\text{CO})_3\text{Br}\{\kappa^2\text{N,N}'\text{-OP}(\text{1,2,3-Tz}^1\text{-Ph})_3\}]$ (1) and $[\text{Re}(\text{CO})_3\{\kappa^2\text{N,N}'\text{-OP}(\text{1,2,3-Tz}^1\text{-Ph})_3\}]\text{Br}$ (4).

	1	4
Re1-N3	2.186(5)	2.180(3)
Re1-N23	2.199(5)	2.187(3)
Re1-Br1/N43	2.5837(8)	2.186(3)
C10-Re1-C20	89.9(2)	90.1(2)
C10-Re1-C30	88.9(2)	87.7(2)
C10-Re1-N3	175.4(2)	177.4(2)
C10-Re1-N23	92.1(2)	93.9(2)
C10-Re1-Br1/N43	91.4(2)	96.8(2)
C20-Re1-C30	88.0(2)	90.3(2)
C20-Re1-N3	92.7(2)	92.4(2)
C20-Re1-N23	175.9(2)	174.9(2)
C20-Re1-Br1/N43	91.7(2)	93.6(2)
C30-Re1-N3	95.0(2)	92.4(2)
C30-Re1-N23	95.6(2)	92.9(2)
C30-Re1-Br1/N43	179.6(2)	174.0(2)
N3-Re1-N23	85.1(2)	83.6(1)
N3-Re1-Br1/N43	84.7(1)	83.0(1)
N23-Re1-Br1/N43	84.7(1)	92.9(1)

conditions are applied. A reaction between $[\text{Re}(\text{CO})_5\text{Br}]$ and $\text{OP}(\text{1,2,3-Tz}^1\text{-benz})_3$ in boiling toluene gives $[\text{Re}(\text{CO})_3\{\kappa^2\text{N,N}'\text{-OP}(\text{1,2,3-Tz}^1\text{-benz})_3\}]\text{Br}$ (4) in moderate yields, while similar attempts with the phenyl-substituted ligand were less successful and a considerable degree of ligand degradation was observed spectroscopically. A small amount of single crystals of $[\text{Re}(\text{CO})_3\{\kappa^2\text{N,N}'\text{-OP}(\text{1,2,3-Tz}^1\text{-Ph})_3\}][\text{Re}_2(\text{CO})_6(\mu\text{-X})_3]$ (3) (X = Br, Cl) could be isolated from a corresponding reaction in CH_2Cl_2 after the addition of $\text{Ag}(\text{PF}_6)$.

The formation of the $[\text{Re}_2(\text{CO})_6(\mu\text{-X})_3]^-$ counter ion in the presence of Ag^+ ions was unexpected, but underlines the remarkable stability of complexes with anionic ligands bridging two $\{\text{M}(\text{CO})_3\}^+$ units (M = Re, Tc), which has also been found for a number of other examples.^[42–48] Even a precedent with mixed Cl^-/Br^- bridging ligands can be found.^[49] An approximate Br^-/Cl^- ratio of 1:1 was derived for the $[\text{Re}_2(\text{CO})_6(\mu\text{-X})_3]^-$ counter ions from a disorder refinement of the halides in the obtained single crystals. Decomposition of CH_2Cl_2 is regarded as the Cl^- source as has been found for the formation of the $[\text{Re}(\text{CO})_3\text{X}\{\kappa^2\text{N,N}'\text{-OP}(\text{1,2,3-Tz}^1\text{-benz})_3\}]$ (X = Cl, Br) (2) complexes.

A single crystal structure determination on $[\text{Re}(\text{CO})_3\{\kappa^2\text{N,N}'\text{-OP}(\text{1,2,3-Tz}^1\text{-Ph})_3\}][\text{Re}_2(\text{CO})_6(\mu\text{-X})_3]$ (X = Br, Cl) (3) clearly confirms the composition of the complex cation with the $\text{OP}(\text{1,2,3-Tz}^1\text{-Ph})_3$ ligand in tripodal coordination. Details of the crystallographic data shall not be discussed here because of the uncertainties caused by the halide disorder in the counter ion. However, a structural plot and a table with some bond lengths and angles of the complex cation can be found in the Supporting Information.

In contrast to the cationic complex with $\text{OP}(\text{1,2,3-Tz}^1\text{-Ph})_3$, the analogous compound $[\text{Re}(\text{CO})_3\{\kappa^2\text{N,N}'\text{-OP}(\text{1,2,3-Tz}^1\text{-benz})_3\}]\text{Br}$ (4) could be isolated in a sufficient amount and studied spectroscopically and by X-ray diffraction. The structure of the complex cation is shown in Figure 3b. Selected bond lengths and angles are compared with the corresponding values in $[\text{Re}(\text{CO})_3\text{Br}\{\kappa^2\text{N,N}'\text{-OP}(\text{1,2,3-Tz}^1\text{-Ph})_3\}]$ (1) in Table 1. The tripodal coordination of the tris(triazolyl)phosphine oxide does not cause considerable changes in bond lengths and angles. Nevertheless, the increase of the symmetry of the coordination sphere can be detected spectroscopically. The IR spectrum of $[\text{Re}(\text{CO})_3\{\kappa^2\text{N,N}'\text{-OP}(\text{1,2,3-Tz}^1\text{-benz})_3\}]\text{Br}$ (4) clearly shows the expected two bands for the $\{\text{Re}(\text{CO})_3\}^+$ core, while one of the band is split in the lower-symmetric $[\text{Re}(\text{CO})_3\text{Br}\{\kappa^2\text{N,N}'\text{-OP}(\text{1,2,3-Tz}^1\text{-Ph})_3\}]$ (1) (*vide supra*).

It is evident that the reactions of $[\text{Re}(\text{CO})_5\text{Br}]$ with the two tris(triazolyl)phosphine oxides of this study are not straightforward and result in a variety of products, from which only a few could be isolated with low to medium yields. Attempted reactions starting from $(\text{NEt}_4)_2[\text{Re}(\text{CO})_5\text{Br}_3]$, which is frequently used as a precursor for the synthesis of tricarbonylrhenium(I) compounds and is best suitable to mimic reactions with the analogous technetium complex $(\text{NEt}_4)_2[\text{Tc}(\text{CO})_5\text{Cl}_3]$,^[54] did not give higher yields and/or more pure products. With respect to the ^{31}P NMR spectra of the reaction mixtures, it cannot be excluded that also (most probably metal-induced) phosphorus-carbon bond breaks play a role. Such hydrolytic degradation of the phosphine oxides has been observed earlier during reactions of $\text{OP}(\text{1,2,3-Tz}^1\text{-R})_3$ ligands with oxorhenium(V) com-

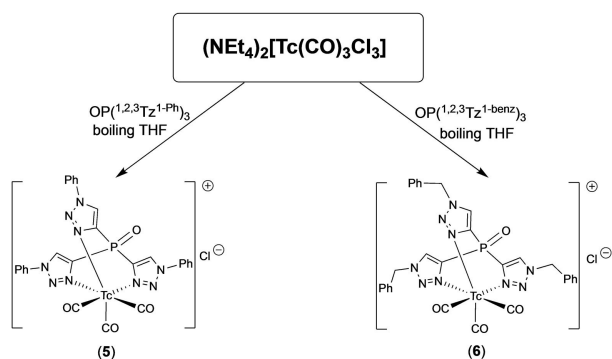
plexes and products with coordinated dihydroxyphosphoranes or diarylphosphinic acids were isolated.^[50]

In contrast to the reactions with tricarbonylrhenium(I) complexes, corresponding experiments with $(\text{NEt}_4)_2[\text{Tc}(\text{CO})_3\text{Cl}_3]$ gave the cationic products with tripodal coordinated $\text{OP}^{(1,2,3)\text{Tz}^{1-\text{Ph}}}_3$ or $\text{OP}^{(1,2,3)\text{Tz}^{1-\text{benz}}}_3$ as pure compounds and with satisfactory yields (Scheme 2). During reactions in boiling THF or at room temperature, there was no evidence for the formation of considerable amounts of neutral $[\text{Tc}(\text{CO})_3\text{Cl}\{\kappa^3\text{N},\text{N}'\text{-OP}^{(1,2,3)\text{Tz}^{1-\text{R}}}_3\}]$ complexes. Reactions at lower temperature have not been performed. The differences between the rhenium and technetium complexes can be understood by the commonly faster reaction kinetics of the 4d element technetium compared with its heavier congener and has been observed for a number of reactions before.^[51–53]

The IR and NMR data of the two technetium complexes are unexceptional and similar to those obtained for the related rhenium compounds. Their ^{99}Tc NMR resonances appear at -1050 ppm ($[\text{Tc}(\text{CO})_3\{\kappa^3\text{N},\text{N}',\text{N}''\text{-OP}^{(1,2,3)\text{Tz}^{1-\text{Ph}}}_3\}]\text{Cl}$ (5)) and at -1023 ppm ($[\text{Tc}(\text{CO})_3\{\kappa^3\text{N},\text{N}',\text{N}''\text{-OP}^{(1,2,3)\text{Tz}^{1-\text{benz}}}_3\}]\text{Cl}$ (6)) relative to TcO_4^- . The observed chemical shifts are in the range, where also the signal for $[\text{Tc}(\text{CO})_3\{\text{hydridotris}(\text{pyrazolyl})\text{borate}\}]$ (-1187 ppm) appears.

Both technetium compounds were studied by single crystal X-ray crystallography. Figure 4 shows ellipsoid representations of their complex cations. Selected bond lengths and angles are summarized in Table 2.

In general, the coordination spheres in the technetium complexes are very similar to that in $([\text{Re}(\text{CO})_3\{\kappa^3\text{N},\text{N}',\text{N}''\text{-OP}^{(1,2,3)\text{Tz}^{1-\text{benz}}}_3\}]\text{Br}$ (4)). The $\text{Tc}-\text{N}$ bond lengths are almost equal and slight deviations from 90° are observed for adjacent $\text{C}-\text{Tc}-\text{N}$ angles, which can be explained by some steric restrictions due to the tripodal coordination of the tris(triazoyl)phosphine oxides. Similar findings have been reported for the structures of $[\text{RhCl}_3\{\kappa^3\text{N},\text{N}',\text{N}''\text{-OP}^{(1,2,3)\text{Tz}^{1-\text{Ph}}}_3\}]$ and tricarbonylmanganese complexes with tris(imidazolyl)phosphines and their chalcogenides.^[38,39]



Scheme 2. Reactions starting from $(\text{NEt}_4)_2[\text{Tc}(\text{CO})_3\text{Cl}_3]$ and their products.

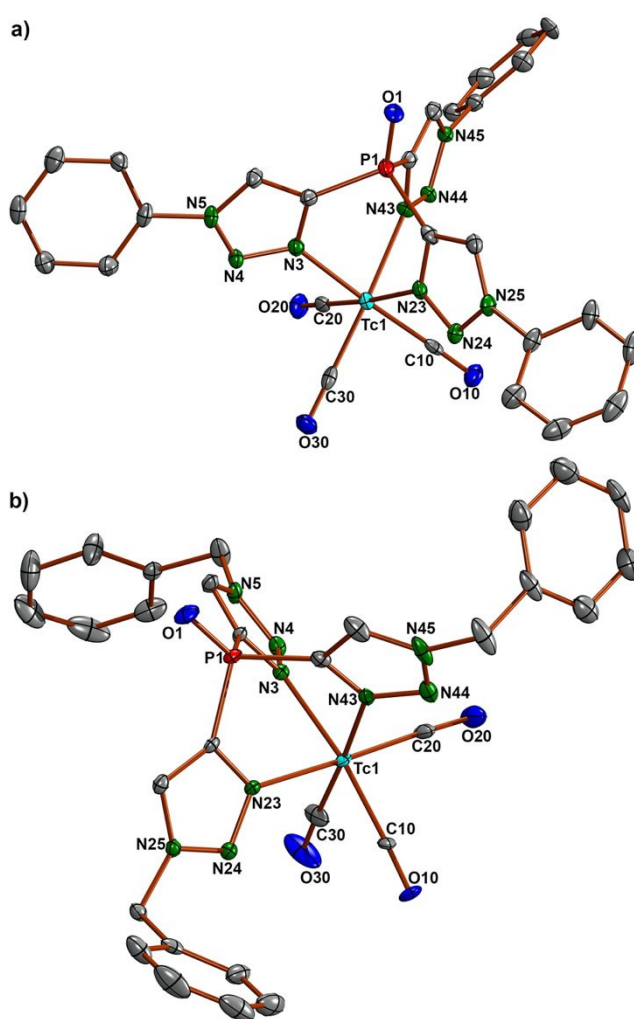


Figure 4. Ellipsoid representation of the structures of the cations of a) $[\text{Tc}(\text{CO})_3\{\kappa^3\text{N},\text{N}',\text{N}''\text{-OP}^{(1,2,3)\text{Tz}^{1-\text{Ph}}}_3\}]\text{Cl}$ (5) and b) $[\text{Tc}(\text{CO})_3\{\kappa^3\text{N},\text{N}',\text{N}''\text{-OP}^{(1,2,3)\text{Tz}^{1-\text{benz}}}_3\}]\text{Cl}$ (6). Thermal ellipsoids represent 50 per cent probability. Hydrogen atoms are omitted for clarity.

Conclusions

Considerable differences have been observed for reactions between tris(triazoyl)phosphine oxide ligands and common tricarbonylrhenium(I) and -technetium(I) precursors. While stable technetium complexes with tripodal coordinated $\text{OP}^{(1,2,3)\text{Tz}^{1-\text{R}}}_3$ ligands are readily formed, reactions with tricarbonylrhenium(I) complexes deliver the corresponding products only with low yields and the formation of a variety of less defined side-products dominates.

The results represent another example, which questions the paradigm that reactions with similar rhenium compounds are sufficient to predict the reactivity of analogous technetium compounds. Whenever possible, reactions with the long-lived $^{99\text{m}}\text{Tc}$ are recommended on the way to corresponding $^{99\text{m}}\text{Tc}$ compounds for nuclear medical procedures. The tris(triazoyl)-phosphine oxide ligands of the present study will be regarded for such studies in the near future in our laboratory, since their

Table 2. Selected bond lengths (Å) and angles (°) in [Tc(CO)₃{κ³N,N',N''-OP(1,2,3-Tz^{1-Ph})₃}Cl] (5) and [Tc(CO)₃{κ³N,N',N''-OP(1,2,3-Tz^{1-benz})₃}Cl] (6).

	5	6
Tc1-N3	2.180(5)	2.186(3)
Tc1-N23	2.189(5)	2.170(3)
Tc1-N43	2.192(5)	2.175(3)
C10-Tc1-C20	88.9(3)	90.2(7)
C10-Tc1-C30	88.9(3)	79.8(4)
C10-Tc1-N3	174.7(2)	172.2(5)
C10-Tc1-N23	91.3(2)	91.0(6)
C10-Tc1-N43	94.3(2)	101.4(3)
C20-Tc1-C30	89.3(2)	89.7(2)
C20-Tc1-N3	96.2(2)	95.4(2)
C20-Tc1-N23	175.4(2)	177.5(2)
C20-Tc1-N43	90.7(2)	93.3(2)
C30-Tc1-N3	92.4(2)	94.9(2)
C30-Tc1-N23	94.8(2)	92.8(2)
C30-Tc1-N43	176.7(2)	176.8(2)
N3-Tc1-N23	83.4(2)	83.6(1)
N3-Tc1-N43	84.3(2)	83.7(1)
N23-Tc1-N43	84.6(2)	84.2(1)

ready synthesis via 'Click' reactions will allow the introduction of a variety of biologically active substituents in their periphery.

Experimental Section

Materials

All chemicals were reagent grade and used without further purification. The syntheses of the following starting materials have been prepared by published procedures: (NEt₄)₂[Tc(CO)₃Cl₃]^[54] [Re(CO)₅Br]^[55] tris(ethynyl)phosphine oxide, benzylazide, OP(1,2,3-Tz^{1-Ph})₃ and OP(1,2,3-Tz^{1-benz})₃.^[39,50,56]

Physical Measurements

The IR spectra of Tc compounds were recorded on a Shimadzu FTIR 8300 spectrometer. All other IR spectra were measured on a Nicolet iS10 FT-IR spectrometer. NMR spectra were recorded at 298 K on a JEOL 400 MHz spectrometer. ESI-MS data were measured on an Agilent 6210 ESI-TOF mass spectrometer (Agilent Technologies, Santa Clara, CA, USA). Spray voltage was set to 4 kV. The solvent flow rate was adjusted to 4 μL/min. The drying gas flow rate was set to 15 psi (1 bar). All other parameters were adjusted for a maximum abundance of the relative ions. All MS results are given in the form: m/z, assignment. Elemental analyses (CHN) were performed on a Heraeus Vario EL elemental analyzer from Elementar Analysensysteme GmbH. The technetium contents of the samples were measured by a HIDEK 300 SL liquid scintillation counter.

Radiation Precautions

⁹⁹Tc is a long-lived β⁻ emitter (E_{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 ⁹⁹Tc are handled. All manipulations were done in a laboratory approved for the handling of radioactive materials.

Syntheses

[Re(CO)₃Br{κ²N,N'-OP(1,2,3-Tz^{1-Ph})₃}] (1)

[Re(CO)₅Br] (40 mg, 0.1 mmol) and OP(1,2,3-Tz^{1-Ph})₃ (48 mg, 0.1 mmol) were dispersed in chloroform and heated under reflux for 24 hours. Hexane was added to the resulting clear solution, which gave a colorless precipitate. The precipitate was filtered off and recrystallized from CH₂Cl₂/MeOH giving colorless single crystals suitable for X-ray diffraction. Yield: 21 mg (21%). Elemental analysis calcd for C₂₇H₁₈N₉O₄PreBr·1/2 CH₃OH: C: 39.1, H: 2.6%. Found C: 39.1, H: 3.0%. ¹H NMR (CD₂Cl₂, ppm): 8.98 (s, 2H, C=C-H), 8.27 (s, 1H, C=C-H), 7.51–7.87 (m, 15H, Ph-H). ³¹P NMR (CDCl₃): -8.2 ppm. IR (cm⁻¹): 2031 (CO), 1931 (CO), 1898 (CO), 1260 (P=O). ESI+MS: m/z = 750.0680 [M-Br]⁺ (calcd for [C₂₇H₁₈N₉O₄Pre]⁺: 750.0771).

[Re(CO)₃{κ³N,N',N''-OP(1,2,3-Tz^{1-benz})₃}Br] (4)

[Re(CO)₅Br] (20 mg, 0.05 mmol) and OP(1,2,3-Tz^{1-benz})₃ (26 mg, 0.05 mmol) were dispersed in toluene and heated under reflux for 90 mins. During this time, the suspension turned clear. Hexane was added to the resulting mixture to give a colorless precipitate. The precipitate was filtered off and recrystallized from CH₂Cl₂/hexane. Colorless crystals. Yield: 22 mg (50%). Elemental analysis calcd for C₃₀H₂₄BrN₉O₄Pre: N: 14.5, C: 40.6, H: 2.7%; found: N: 14.2, C: 41.9, H: 3.4%. ¹H NMR (CDCl₃, ppm): 9.17 (s, 3H, C=C-H), 7.30–7.56 (m, 15H, Ph-H), 5.88 (m, 6H, -CH₂-). ³¹P NMR (CD₂Cl₂): -11.2 ppm. IR (cm⁻¹): 2042 (CO), 1933 (CO), 1259 (P=O). ESI+MS: m/z = 792.1230 [M]⁺ (calcd for [C₃₀H₂₄N₉O₄Pre]⁺: 792.1246).

[Tc(CO)₃{κ³N,N',N''-OP(1,2,3-Tz^{1-Ph})₃}Cl] (5)

(NEt₄)₂[Tc(CO)₃Cl₃] (55 mg, 0.1 mmol) was dissolved in 2 mL of THF and OP(1,2,3-Tz^{1-Ph})₃ (48 mg, 0.1 mmol) in 3 mL THF was added. The mixture was stirred at room temperature for 1 h. After the removal of the solvent in vacuum, the residue was extracted with 2.5 mL of CH₂Cl₂. Methanol (2.5 mL) was added and the clear solution was stored in a refrigerator for slow evaporation. Yellow single crystals. Yield: 50 mg (72%). Elemental analysis calcd for C₂₇H₁₈ClN₉O₄PTc: Tc 14.2%; found: Tc 14.4%. ¹H NMR (CDCl₃, ppm): 8.89 (s, 3H, C=C-H), 7.77–7.25 (m, 15H, Ph-H). ³¹P NMR (CDCl₃): -5.4 ppm. ⁹⁹Tc NMR (CDCl₃): -1050 ppm, Δν_{1/2} = 1680 Hz. IR (cm⁻¹): 2041 (CO), 1944 (CO), 1233 (P=O).

[Tc(CO)₃{κ³N,N',N''-OP(1,2,3-Tz^{1-benz})₃}Cl] (6)

(NEt₄)₂[Tc(CO)₃Cl₃] (55 mg, 0.1 mmol) was dissolved in 2 mL of THF and OP(1,2,3-Tz^{1-benz})₃ (52 mg, 0.1 mmol) in 3 mL THF was added. The mixture was heated on reflux for 2 h. The volume of the solvent was reduced to 2 mL and n-hexane (2 mL) was added. A yellow solid precipitated upon slow evaporation of the solvents. Single crystals for X-ray diffraction were grown from CH₂Cl₂/MeOH. Yield: 45 mg (61%). Elemental analysis calcd for C₃₀H₂₄ClN₉O₄PTc: Tc 13.4%; found: Tc 13.8%. ¹H NMR (CDCl₃, ppm): 8.20 (s, 3H, C=C-H), 7.77–7.29 (m, 15H, Ph-H), 5.56 (s, 6H, -CH₂-). ³¹P NMR (CDCl₃): -9.5 ppm. ⁹⁹Tc NMR (CDCl₃): -1023 ppm, Δν_{1/2} = 520 Hz. IR (cm⁻¹): 2050 (CO), 1954 (CO), 1240 (P=O).

X-ray Crystallography

The intensities for the X-ray diffraction studies were recorded on a Bruker D8 Venture instrument with Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). The space groups were determined from systematic absences. Structure solutions and refinements were performed with the SHELX program package.^[57,58] Absorption corrections were done with SADABS.^[59] 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.^[60] More details about the analyses are contained in the Supporting Information.

Deposition Numbers 2052549, 2052550, 2052551 and 2052552 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.

Acknowledgements

L. B. gratefully acknowledges a Ph.D. scholarship from the Chinese Scholarship Council (CSC). This work was done with the assistance of the Core Facility BioSupraMol supported by the DFG. Open access funding enabled and organized by Projekt DEAL.

Keywords: tris(azoyl)phosphine oxides · tricarbonylrhenium(I) · tricarbonyltechnetium(I) · tripod ligands

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Manuscript received: January 8, 2021

Revised manuscript received: February 18, 2021

Accepted manuscript online: February 21, 2021