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-1H-1,2,3-triazol-4-yl)phosphine oxide (OP(1,2,3-Tz3−Ph)) and tris(1-benzyl-1H-1,2,3-triazol-4-yl)phosphine oxide (OP(1,2,3-Tz3−Ben)), were used in reactions with [Re(CO)Br] and (NEt3)2[Tc(CO)Cl2]. While the formation of rhenium complexes with bidentate and tridentate coordinated phosphine oxides was observed, for technetium only cationic complexes with tripodal coordinated OP(1,2,3-Tz3−) ligands were isolated. The products have been characterized spectroscopically and by single crystal X-ray diffraction.

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(ethylendiy)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(1,2,3-Tz3−Ph)3 in high purity and with a yield of 95 per cent.

Reactions of [Re(CO)Br] with OP(1,2,3-Tz3−Ph)3 or OP-(1,2,3-Tz3−Ben)3 in boiling CHCl3 result in the replacement of two carbonyl ligands and the formation of [Re(CO)Br(OP(1,2,3-Tz3−Ph))2] complexes (Scheme 1). Remarkably, these reactions are not

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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 99mTc 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 = 99mTc, 188Re) cations, which are perfect precursors for nuclear medical applications.[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.[14,15–20] 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(mercaptopimidazolyl)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-1H-1,2,3-triazol-4-yl)phosphine oxide, OP(1,2,3-Tz3−Ph)3 and tris(1-benzyl-1H-1,2,3-triazol-4-yl)phosphine oxide, OP-(1,2,3-Tz3−Ben)3 (Figure 1).

Figure 1. Tris(1,2,3-triazolyl)phosphine oxides used in the present study.
Scheme 1. Reactions preformed starting from [Re(CO)₅Br] 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 [Re(CO)₅Br]₄[x,N,N'-OP(¹²,²-T₂⁻-benz)] (1), while during the analogous reaction with OP(¹²,²-T₂⁻-benz) chloride abstraction from the solvent CHCl₃ and the formation of considerable amounts of the corresponding chlorido complex [Re(CO)₅Cl[x,N,N'-OP(¹²,²-T₂⁻-benz)]] (2b) was observed. This Br/Cl exchange was not an accidental effect of one single reaction mixture, but has been found to be systematical. Although NMR and IR spectroscopy give no safe evidence for the formation of a mixture of the very similar compounds [Re(CO)₅Br[x,N,N'-OP(¹²,²-T₂⁻-benz)]] (2a) and [Re(CO)₅Cl[x,N,N'-OP(¹²,²-T₂⁻-benz)]] (2b), the presence of considerable amounts of both compound 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 [Re(CO)₅X[x,N,N'-OP(¹²,²-T₂⁻-benz)]] (2) (X=Cl, 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 [Re(CO)₅Br[x,N,N'-OP(¹²,²-T₂⁻-phen)]] (1), which is depicted in Figure 3a. Selected bond lengths and angles are summarized in Table 1.

The coordination sphere of rhenium in [Re(CO)₅Br[x,N,N'-OP(¹²,²-T₂⁻-phen)]] (1) is an only slightly distorted octahedron. Some marginal deviations from the ideal 90° and 180° angles are due to the chelate formation of the phosphate oxide. But obviously, the bidentate coordination of this ligands does not cause a considerably steric stress.

The ³¹P NMR spectrum of the complex shows a single resonance at -8.2 ppm in CDCl₃, which is only a slight shift compared to the uncoordinated ligand (-5.7 ppm). In the (+)-ESI mass spectrum of [Re(CO)₅Br[x,N,N'-OP(¹²,²-T₂⁻-phen)]] (1), there is no evidence for a Br/Cl exchange as has been observed for the corresponding complex with OP(¹²,²-T₂⁻-benz). The molecular ion region of the spectrum shows one intense signal at m/z = 750.068, which can clearly be assigned to the [M-Br]+ ion. The non-symmetric coordination sphere of the rhenium atom in [Re(CO)₅Br[x,N,N'-OP(¹²,²-T₂⁻-phen)]] (1) is well reflected by the appearance of three CO vibrations at 1898, 1931 and 2031 cm⁻¹. The formation of cationic [Re(CO)₅[x,N,N'-OP(¹²,²-T₂⁻-phen)]$^+$ complexes can be achieved when more drastic reaction
conditions are applied. A reaction between [Re(CO)]Br and OP(\(1,2,3\)-Tz\(_2\)-benz)\(_3\) in boiling toluene gives [Re(CO)](\(\kappa^3\)N,N',N'-OP-\(1,2,3\)-Tz\(_2\)-benz\))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 [Re(CO)](\(\kappa^3\)N,N',N'-OP-\(1,2,3\)-Tz\(_2\)-benz\)]\(\mu\)X\(_2\)) (X = Br, Cl) could be isolated from a corresponding reaction in CH\(_2\)Cl\(_2\) after the addition of Ag(PF\(_6\)).

The formation of the [Re(CO)]\(\mu\)X\(_2\) counter ion in the presence of Ag\(^+\) ions was unexpected, but underlines the remarkable stability of complexes with anionic ligands bridging two [M(CO)]\(^+\) units (M = Re, Tc), which has also been found for a number of other examples.\(^{[52-46]}\) Even a precedent with mixed Cl\(^-\)/Br\(^-\) bridging ligands can be found.\(^{[46]}\) An approximate Br\(^-\)/Cl\(^-\) ratio of 1:1 was derived for the [Re(CO)]\(\mu\)X\(_2\) counter ions from a disorder refinement of the halides in the obtained single crystals. Decomposition of CH\(_2\)Cl\(_2\) is regarded as the Cl\(^-\) source as has been found for the formation of the [Re(CO)]X-\(\kappa^3\)N,N'-OP-\(1,2,3\)-Tz\(_2\)-benz\)] (X = Cl, Br) (2) complexes.

A single crystal structure determination on [Re(CO)](\(\kappa^3\)OP-\(1,2,3\)-Tz\(_2\)-benz\)]\(\mu\)X\(_2\)) (X = Br, Cl) (3) clearly confirms the composition of the complex cation with the OP(\(1,2,3\)-Tz\(_2\)-benz)\(_3\)) ligand in triadop 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 OP(\(1,2,3\)-Tz\(_2\)-benz)\(_3\)), the analogous compound [Re(CO)](\(\kappa^3\)N,N,N'-OP-\(1,2,3\)-Tz\(_2\)-benz\)]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 [Re(CO)]Br(\(\kappa^3\)N,N'-OP-\(1,2,3\)-Tz\(_2\)-benz\)] (1) in Table 1. The triadop 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 [Re(CO)]Br(\(\kappa^3\)N,N'-OP-\(1,2,3\)-Tz\(_2\)-benz\)] (4) clearly shows the expected two bands for the [Re(CO)]\(^+\) core, while one of the band is split in the lower-symmetric [Re(CO)]Br(\(\kappa^3\)N,N'-OP-\(1,2,3\)-Tz\(_2\)-benz\)] (vide supra).

It is evident that the reactions of [Re(CO)]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 (NET\(_3\))[Re(CO)]Br\(_2\)], which is frequently used as a precursor for the synthesis of tricarbonylre(hium(I) compounds and is best suitable to mimic reactions with the analogous technetium complex (NET\(_3\))[Tc(CO)]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 OP(\(1,2,3\)-Tz\(_2\)-benz\)\(_3\)) ligands with oxorhenium(V) com-

Table 1. Selected bond lengths (Å) and angles (°) in [Re(CO)]Br(\(\kappa^3\)N,N,N'-OP-\(1,2,3\)-Tz\(_2\)-benz\)] (1) and [Re(CO)](\(\kappa^3\)N,N',N'-OP-\(1,2,3\)-Tz\(_2\)-benz\)]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-Rel-C20| 89.9(2)   | 90.1(2)    |
| C10-Rel-C30| 88.9(2)   | 87.7(2)    |
| C10-Rel-N3| 175.4(2)  | 177.4(2)   |
| C10-Rel-N23| 92.1(2)   | 93.9(2)    |
| C10-Rel-Br1/N43| 91.4(2) | 96.8(2)    |
| C20-Rel-C30| 88.0(2)   | 90.3(2)    |
| C20-Rel-N3| 92.7(2)   | 92.4(2)    |
| C20-Rel-N23| 175.9(2)  | 174.9(2)   |
| C20-Rel-Br1/N43| 91.7(2) | 93.6(2)    |
| C30-Rel-N3| 95.0(2)   | 92.4(2)    |
| C30-Rel-N23| 95.6(2)   | 92.9(2)    |
| C30-Rel-Br1/N43| 179.6(2) | 174.0(2)   |
| N3-Rel-N23| 85.1(2)   | 83.6(1)    |
| N3-Rel-Br1/N43| 84.7(1)   | 83.0(1)    |
| N23-Rel-Br1/N43| 84.7(1)  | 92.9(1)    |
plexes and products with coordinated dihydroxyphosphoranes or diarylphosphinic acids were isolated.\(^{56}\)

In contrast to the reactions with tricarbonylrhenium(I) complexes, corresponding experiments with (NEt\(_2\))\(_2\)Tc(CO)\(_3\)Cl\(_3\) gave the cationic products with tripodal coordinated OP-\((1,2,3-Tz)\)\(_{\text{R}}\) or OP-\((1,2,3-Tz)\)\(_{\text{R}}\) 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 [Tc(CO)\(_3\){k\(_N\),N\(_N\),N\(_N\)-OP(1,2,3-Tz)\(_{\text{R}}\)}] 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 \(^{99m}\)Tc NMR resonances appear at \(-1050 \text{ ppm} \) ([Tc(CO)\(_3\){k\(_N\),N\(_N\),N\(_N\),OP(1,2,3-Tz)\(_{\text{R}}\)}]Cl \((5)\)) and at \(-1023 \text{ ppm} \) ([Tc(CO)\(_3\){k\(_N\),N\(_N\),N\(_N\),OP(1,2,3-Tz\(_{\text{R}}\))}]Cl \((6)\)) relative to TcO\(_3^+\). The observed chemical shifts are in the range, where also the signal for [Tc(CO)\(_3\){hydridotris(pyrazolyl)borate}] (\(-1187 \text{ ppm}\)) 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 ([Re(CO)\(_3\){k\(_N\),N\(_N\),N\(_N\)-OP(1,2,3-Tz)\(_{\text{R}}\)}]Br \((4)\)). The Tc-N bond lengths are almost equal and slight deviations from 90° are observed for adjacent C-Tc-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 [RhCl\(_2\){k\(_N\),N\(_N\),N\(_N\)-OP(1,2,3-Tz)\(_{\text{R}}\)}] and tricarbonylmanganese complexes with tris(imidazoyl)phosphines and their chalcogenides.\(^{38,39}\)

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 OP-\((1,2,3-Tz)\)\(_{\text{R}}\) 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 \(^{99m}\)Tc are recommended on the way to corresponding \(^{99m}\)Tc compounds for nuclear medical procedures. The tris(triazoyl)-phosphate oxide ligands of the present study will be regarded for such studies in the near future in our laboratory, since their

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**Figure 4. Ellipsoid representation of the structures of the cations of**

a) [Tc(CO)\(_3\){k\(_N\),N\(_N\),N\(_N\),OP(1,2,3-Tz)\(_{\text{R}}\)}]Cl \((5)\) and b) [Tc(CO)\(_3\){k\(_N\),N\(_N\),N\(_N\)-OP(1,2,3-Tz)\(_{\text{R}}\)}]Cl \((6)\). Thermal ellipsoids represent 50 per cent probability. Hydrogen atoms are omitted for clarity.

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**Scheme 2. Reactions starting from (NEt\(_2\))\(_2\)Tc(CO)\(_3\)Cl\(_3\) and their products.**

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counter. Samples were measured by a HIDEX 300 SL liquid scintillation spectrometer. All other IR spectra were measured on a Nicolet 7000 FTIR spectrometer. Tc(I) compounds were recorded on a Shimadzu FTIR spectrometer. All other parameters were adjusted for a better signal-to-noise ratio and a resolution of 2 cm⁻¹. The IR spectra of Tc compounds were recorded on a Shimadzu FTIR spectrometer.

### Syntheses

[Re(CO)₃Br(x′N,N′-OP(1,2-Tz⁻⁻⁻⁻)])] (1)

[Re(CO)₃Br] (40 mg, 0.1 mmol) and OP(1,2-Tz⁻⁻⁻⁻) (48 mg, 0.1 mmol) were dissolved in chloroform and heated under reflux for 24 hours. The 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 C₁₇H₁₃N₃O₋₁: 75.1–7.87 (m, 15H, Ph–H). ³⁵P 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 [C₁₂H₆N₃O⁻PBr]⁻: 750.0771).

[Re(CO)₃Br(x′N,N′-OP(1,2-Tz⁻⁻⁻⁻)])Br (4)

[Re(CO)₃Br] (20 mg, 0.05 mmol) and OP(1,2-Tz⁻⁻⁻⁻) (26 mg, 0.05 mmol) were dispersed in toluene and heated under reflux for 90 mins. During this time, the suspension turned clear. The 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 C₁₇H₁₂BrN₃O₃PBr: 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–H), 7.30–7.56 (m, 15H, Ph–H), 5.88 (m, 6H, –CH₃) ppm. ³¹P NMR (CDCl₃): −11.2 ppm. IR (cm⁻¹): 2042 (CO), 1933 (CO), 1259 (P=O). ESI + MS: m/z = 792.1230 [M]⁺ (calcd for [C₁₀H₁₃N₃O⁺P]⁻: 792.1246).

### 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: (NEt₃)[Tc(CO)₅Cl] (54) [Re(CO)₃Br] (56) tris(ethynyl)phosphine oxide, benzylazide, OP(1,2-Tz⁻⁻⁻⁻) and OP(1,2-Tz⁻⁻⁻⁻)Br (55).

#### 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. Element 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 HiDEX 300 SL liquid scintillation counter.

#### Radiation Precautions

⁹⁹Tc is a long-lived β⁻ emitter (Eᵥmax = 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.

#### Table 2. Selected bond lengths (Å) and angles (°) in [Tc(CO)₅(x′N,N′-OP(1,2-Tz⁻⁻⁻⁻))]Cl (5) and [Tc(CO)₅(x′N,N′-OP(1,2-Tz⁻⁻⁻⁻)])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) | 87.9(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) |
X-ray Crystallography

The intensities for the X-ray diffraction studies were recorded on a Bruker D8 Venture instrument with Mo Kα radiation (λ = 0.71073 Å). The space groups were determined from systematic absences. Structure solutions and refinements were performed with the SHELX program package. Absorption corrections were done with SADABS. 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. 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.

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