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Triazacyclohexane (tach) Complexes of High-Valent Rhenium: Syntheses of $[(R_3tach)ReO_3]^+$ ($R = -CH_3, -CH_2C_6H_5$) and Its Substitution Reactions

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N-Alkylated derivatives of 1,3,5-triazacyclohexane (tach) are versatile, facially coordinating ligands. We present the syntheses and full characterization of two new complexes of the $[(R_3tach)ReO_3]^+$ type. In these complexes, the tach ligand is readily substituted by bi- and tridentate ligands; hence, they can be considered as sources of the $[ReO_3]^+$ motif for Re^{VII} complexes.

The coordination chemistry of rhenium with 1,4,7-triazacyclononane (tacn) as a ligand is very well developed, and a variety of complexes containing rhenium in the formal oxidation states I+,[1] III+,[2−4] IV+,[4,5] V+,[4,6−8] and VII+[7,9−11] have been described and fully characterized. In contrast to tacn chemistry, complexes containing the smallest member of the triazacycloalkane family, 1,3,5-triazacyclohexane (tach) and N-alkylated derivatives (R_3tach) thereof, are rather rare and do not exist for rhenium and technetium in particular. For the neighboring elements molybdenum and tungsten, Baker et al. reported complexes with 1,3,5-trimethyl-1,3,5-triazacyclohexane (Me_3tach) ligands in $[(Me_3tach)M^0(CO)_3]$ (M = Mo, W). The tach ligand in these complexes is substitution-labile and enables access to a variety of metal carbonyl complexes via displacement reactions of Me_3tach.[12] Furthermore, the low steric demand of the R_3tach ligand is a key feature for the development of homogeneous models ($[(R_3tach)CrCl_3]$) for the Phillips catalyst (CrO_3/SiO_2).[13−15] Similar to tacn, R_3tach can also stabilize high oxidation states. Holm et al. reported Mo^{VI} complexes with R_3tach in order to demonstrate the nucleophilic character of the $[Mo^{VI}O_3]^0$ fragment but left tach untouched.[16]

High-valent rhenium complexes comprising the *fac*-$[ReO_3]^+$ motif with monodentate ligands have been of interest for catalytic applications for a long time.[17] More recently, a strategy for radiolabeling of biomolecules via [3 + 2] cycloadditions of $[^{99m}TcO_3]^+$-based complexes with alkenes was reported.[18] In this context, stable $[ReO_3]^+$ analogues with tridentate ligands are of interest as nonradioactive reference complexes.

Herein, we report the syntheses, structural characterizations, and substitution properties of the two Re^{VII} complexes $[(Me_3tach)ReO_3][ReO_4]$ (**1**$[ReO_4]$) and $[(Bn_3tach)ReO_3][ReO_4]$ (**2**$[ReO_4]$; Bn_3tach = 1,3,5-tribenzyl-1,3,5-triazacyclohexane; Chart 1) and their ligand replacement reactions.

Under inert conditions, the common starting material $[Re_2O_7]$ reacts very rapidly with Me_3tach or Bn_3tach in tetrahydrofuran (THF) or a mixture of THF and Et_2O to yield **1**$[ReO_4]$ and **2**$[ReO_4]$. The two complexes were received as colorless powders in 76% and 86% yield, respectively. Recrystallization from CH_3CN or THF produced air-stable colorless plates, suitable for X-ray diffraction analysis. The crystal structure of $\mathbf{1}^+$ is shown in Figure 1, and that of $\mathbf{2}^+$ is given in the Supporting Information (SI).

In $\mathbf{1}^+$ and $\mathbf{2}^+$, three oxygen and three nitrogen atoms are coordinated to the rhenium center, which is in a strongly distorted octahedral environment. Because of the formation of a four-membered ring (Re−N−C−N), the N−Re−N

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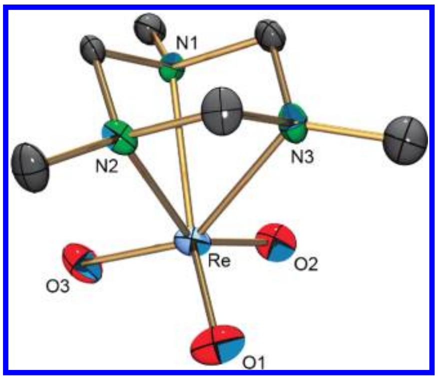
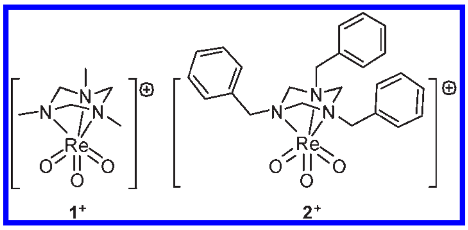


Figure 1. ORTEP representation[19] of the **1**$^+$ cation. Thermal ellipsoids represent 50% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Re−O1 1.707(5), Re−O2 1.708(5), Re−O3 1.709(5), Re−N1 2.262(6), Re−N2 2.276(6), Re−N3 2.264(6); O1−Re−O2 109.6(3), O1−Re−O3 108.7(3), O2−Re−O3 108.6(3), N1−Re−N2 59.9(2), N1−Re−N3 60.4(2), N2−Re−N3 60.5(2).

Chart 1



bond angles are substantially smaller [**1**$^+$, 59.9(2)−60.5(2)°; **2**$^+$, 59.4(2)−60.9(2)°] than that in the corresponding [(tacn)ReO$_3$]$^+$ complex [76.4(2)°].[9] In both complexes, the O−Re−O angles are opened up to 109.6(3)−108.6(3)° for **1**$^+$ and to 108.8(2)−107.6(2)° for **2**$^+$. Bond angles close to the ideal tetrahedral angle are a typical feature for *fac*-[ReO$_3$]$^+$ cores (d^0 systems) and mirror the sterical demand of the Re═O double bonds. All relevant bond lengths and angles of all synthesized [ReO$_3$]$^+$ complexes in this report are summarized in Tables SI2 and SI3 in the SI.

As solids, both complexes **1**[ReO$_4$] and **2**[ReO$_4$] are stable under dry conditions. They are soluble and stable in polar organic solvents but slowly hydrolyze to [ReO$_4$]$^-$ in the presence of water. The $\nu_{Re=O}$ stretching vibrations of **1**$^+$ and **2**$^+$ were observed at 934 and 940 cm^{-1}, respectively, and are in the same region as that in the comparable Re^{VII} complex [(tacn)ReO$_3$][ReO$_4$] (935 cm^{-1}).[10]

On the basis of the reports about substitutions of Me$_3$tach on [(Me$_3$tach)M^0(CO)$_3$] (M = Mo, W),[12] a similar behavior was proposed for [(Me$_3$tach)ReO$_3$]$^+$ because of the isolobal relationship of the [Re(CO)$_3$]$^+$ and [ReO$_3$]$^+$ fragments. To assess the substitution lability of Me$_3$tach, **1**[ReO$_4$] was reacted with a series of bi- and tridentate ligands. The reactions of **1**[ReO$_4$] with 2,2′-bipyridine (bipy), 1,10-phenanthroline-5,6-dione (phd), and tetrapyrido[3,2-α:2′,3′-*c*:3″,2‴-*h*:2‴,3‴-*j*]phenazine (tpphz) lead under moderate conditions and in good yields to the corresponding complexes [(bipy)ReO$_3$Cl] (**3**), [(phd)ReO$_3$Cl] (**4**), and the binuclear compound [(tpphz)(ReO$_3$Br)$_2$] (**5**), respectively (Scheme 1).

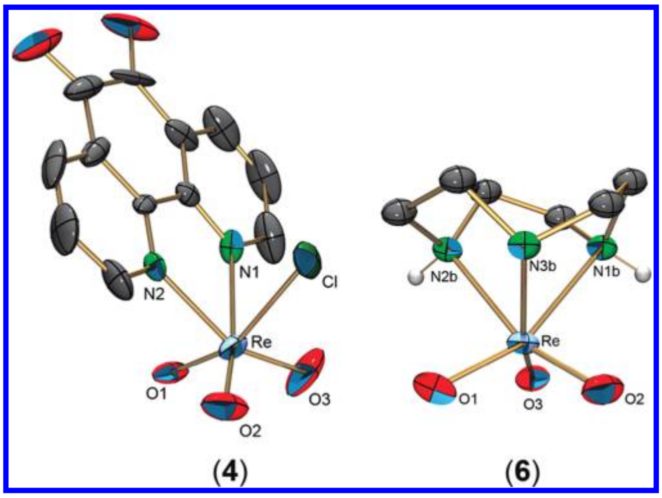
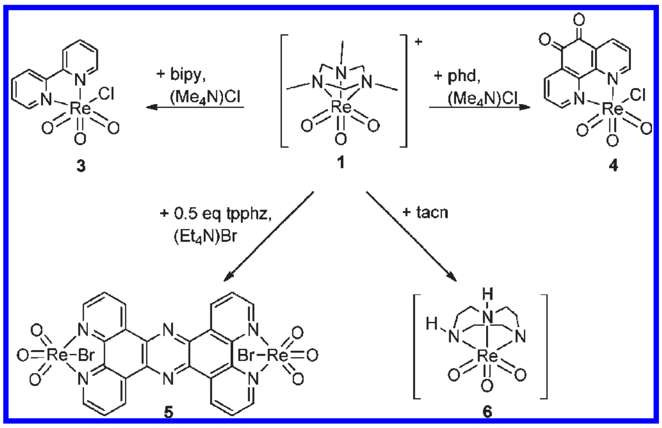


Figure 2. ORTEP representation[19] of **4** and one conformation of the ligand in **6**. Thermal ellipsoids represent 50% probability. Hydrogen atoms are omitted for clarity (except N−H of **6**). Selected bond lengths (Å) and angles (deg) in **4**: Re−O1 1.689(5), Re−O2 1.703(5), Re−O3 1.726(6), Re−N1 2.263(5), Re−N2 2.241(5), Re−Cl 2.455(2); O1−Re−O2 103.8(2), O1−Re−O3 103.6(3), O2−Re−O3 107.5(3), N1−Re−N2 71.4(2), N1−Re−Cl 78.0(2), N2−Re−Cl 75.9(2). Selected bond lengths (Å) and angles (deg) in **6**: Re−O1 1.732(3), Re−O2 1.725(3), Re−O3 1.750(3), Re−N1b 2.32(2), Re−N2b 2.25(2), Re−N3b 2.02(2); O1−Re−O2 108.2(2), O1−Re−O3 103.9(2), O2−Re−O3 103.8(2), N1b−Re−N2b 74.5(4), N1b−Re−N3b 75.9(5), N2b−Re−N3b 76.2(5).

Scheme 1. Ligand Replacement Reactions of **1**$^+$ with Bi- or Tridentate Ligands



Whereas **3** is known and has been fully characterized,[20] complex **4** is new. It was possible to structurally characterize **4** and to confirm its authenticity (Figure 2).

However, because of the complete insolubility of **4** in common organic solvents, crystals were obtained along a different route. TBA[ReO$_4$] was dissolved in benzoyl chloride and layered with a solution of phd in dry MeCN. The slow diffusion of phd into the activated [ReO$_4$]$^-$ (O$_3$ReOCOC$_6$H$_5$) afforded X-ray-quality crystals. A comparison with the IR spectra of **4** received by a substitution reaction from **1**$^+$ and elemental analysis confirmed the identity of the products prepared along the two routes.

With its extensive π system, tpphz belongs to a class of ligands that are under intensive investigation because of their unique feature of forming stable metal complexes with

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interesting excited-state reactivities and redox properties.[21,22] The low solubility of tpphz renders the synthesis of complexes with this ligand difficult. The reactive complex **1**$^+$ reacted in MeCN with suspended tpphz to form **5**. The product **5** precipitated immediately from the reaction solution and formed an insoluble, yellow powder, which was characterized by IR spectroscopy and elemental analysis (see the SI).

The characteristic Re=O vibrations for **3**−**5** were all found between 947 and 943 cm^{-1} (symmetric Re=O vibration), 923 and 919, and 914 and 902 cm^{-1} (asymmetric Re=O vibration), respectively. These are the typical regions for $[ReO_3]^+$ complexes with bidentate ligands.[20]

The reaction of **1**$^+$ with tacn did not directly yield the expected $[(tacn)ReO_3][ReO_4]$. The tacn ligand replaced Me_3tach very rapidly; however, because of the strong basicity of the replaced Me_3tach, the zwitterionic species $[(tacn\text{-}H)ReO_3]$ (**6**) precipitated as a green/yellow powder from the solution. Complex **6**, described by Pomp and Wieghardt,[23] is insoluble in common organic solvents. If **6** is dissolved in water, an equilibrium between **6** and its protonated form **6**$^+$ is established (pK_a = 10.3 for **6**$^+$).[23] Evaporation of such an equilibrated solution leads to exclusive crystallization of **6** as yellow sticks of X-ray quality. The crystal structure of **6** is shown in Figure 2.

In **6**, the rhenium atom is in a distorted octahedral environment of three facially coordinated nitrogen atoms of the macrocyclic ligand and three oxygen atoms. The X-ray structure of **6** shows the deprotonated tacn ligand to be disordered in a ratio of 52:48. The two crystallographic species have very similar structural (λ/δ disorder of the tacn) features. Thus, only one will be discussed in detail. In contrast to the cationic compound $[(tacn)ReO_3][ReO_4]$, the Re−N bond lengths in **6** are not equidistant.[9] Whereas two bond lengths in **6** are longer [2.32(2) and 2.25(2) Å] than that in $[(tacn)ReO_3][ReO_4]$ [2.197(5) Å], the bond length of the deprotonated nitrogen atom to the rhenium atom (Re−N3b) is significantly shorter [2.02(2) Å]. The short Re−N bond also influences the Re=O bond length in the trans position, which is slightly longer [1.750(3) Å] than the Re=O bond lengths trans to the protonated amines [1.732(3) and 1.725(3) Å]. The strongly distorted coordination sphere is mirrored in a complex splitting of the Re=O vibrations (917−845 cm^{-1}, multicomponent band) in the IR spectrum of **6**.[23]

In conclusion, the two new complexes presented here, **1**$[ReO_4]$ and **2**$[ReO_4]$, can be considered as new sources of the $[ReO_3]^+$ motif and pave the way for syntheses of $[Re^{VII}O_3]^+$ complexes by ligand substitution. The synthesis of $[Re^{VII}O_3]^+$ complexes by ligand replacement reactions can complement today's established reaction pathways for the synthesis of $[ReO_3]^+$ complexes, which start directly either from $[Re_2O_7]$ or from complexes in lower oxidation states and subsequently oxidize to Re^{VII}. As a proof of principle, a series of $[ReO_3]^+$ complexes were synthesized following this new synthetic strategy.

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Supporting Information Available: Full synthetic and spectroscopic details for all compounds and crystallographic data for complexes **1**$[ReO_4]$, **2**$[ReO_4]$, **4**, and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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