

Aryl and NHC Compounds of Technetium and Rhenium

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S Supporting Information

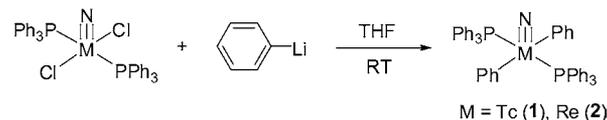
ABSTRACT: Air- and water-stable phenyl complexes with nitridotechnetium(V) cores can be prepared by straightforward procedures. $[\text{TcNPh}_2(\text{PPh}_3)_2]$ is formed by the reaction of $[\text{TcNCl}_2(\text{PPh}_3)_2]$ with PhLi . The analogous N-heterocyclic carbene (NHC) compound $[\text{TcNPh}_2(\text{HL}^{\text{Ph}})_2]$, where HL^{Ph} is 1,3,4-triphenyl-1,2,4-triazol-5-ylidene, is available from $(\text{NBu}_4)[\text{TcNCl}_4]$ and HL^{Ph} or its methoxy-protected form. The latter compound allows the comparison of different Tc–C bonds within one compound. Surprisingly, the Tc chemistry with such NHCs does not resemble that of corresponding Re complexes, where CH activation and orthometalation dominate.

The organometallic chemistry of technetium, particularly the structural chemistry of organotechnetium compounds, is one of the least explored among common transition metals.¹ Of the less than 140 crystallographically studied compounds containing Tc–C bonds (vs ~4500 entries for the corresponding Re compounds), there are less than 20 that do not contain carbonyl or isocyanide ligands.² The focus on the latter compounds can easily be understood with regard to the use of the isocyanide complex $[\text{}^{99\text{m}}\text{Tc}(\text{L})_6]^+$ (R = methoxyisobutyl isonitrile) as a routine myocardial imaging agent in clinical nuclear medicine,³ and the fact that with the development of a kitlike preparation of $[\text{}^{99\text{m}}\text{Tc}(\text{CO})_3(\text{H}_2\text{O})_3]^+$, carbonyl complexes of technetium have shown their potential for radiopharmaceutical imaging.⁴ We recently introduced another class of organometallic technetium compounds: complexes with 1,3-dialkyl-4,5-dimethylimidazol-2-ylidenes.⁵ The fact that these compounds as well as their rhenium analogues are water-stable and can be synthesized by a simple transmetalation approach⁶ encouraged us to get deeper insights into the organometallic chemistry of the first artificial element.

Here we present the syntheses and reactivities of the first phenyl and triazolylidene technetium complexes. The lack of knowledge about aryltechnetium complexes is surprising, given the fact that aryl complexes of all other transition metals are well-known.^{2,7}

The synthesis of the first phenyl complex of technetium was straightforward.⁸ Treatment of $[\text{TcNCl}_2(\text{PPh}_3)_2]$ with 3 equiv of PhLi in dry THF afforded orange-red crystals having the composition $[\text{TcNPh}_2(\text{PPh}_3)_2]$ (**1**) (Scheme 1). The IR spectrum of the complex shows a distinct band at 1092 cm^{-1} for the $\text{Tc}\equiv\text{N}$ vibration. The ^{13}C NMR spectrum exhibits a triplet at 174.4 ppm that can be assigned to the carbon atoms bonded directly to the technetium atom. The crystal structure of **1** shows a five-coordinate complex with distorted trigonal-

Scheme 1. Synthesis of 1 and 2



bipyramidal geometry (Figure 1).⁸ The Tc–C bond lengths are in the same range as those in the Tc^{VI} dimer $[\{\text{Tc}(\text{O})\text{Me}_2\}_2(\mu-$

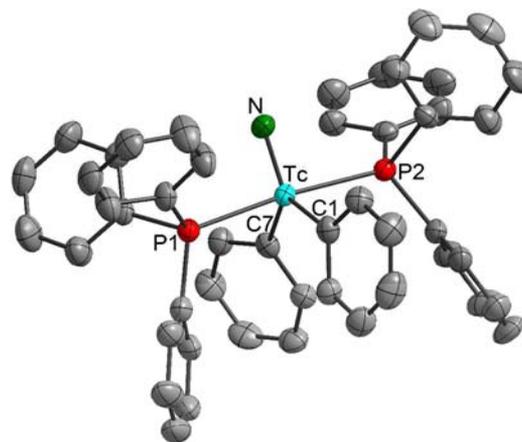


Figure 1. Molecular structure of **1**. The rhenium complex is virtually identical and therefore not shown. H atoms and solvent molecules have been omitted for clarity. Selected bond lengths (Å) and angles (deg) in **1**: Tc–N, 1.628(4); Tc–Cl, 2.138(4); Tc–C7, 2.127(4); P1–Tc–P2, 174.3(1); N–Tc–C1, 118.6(2); C1–Tc–C7, 123.5(2). In **2**: Re–N, 1.660(5); Re–C1, 2.117(4); Re–C7, 2.133(5); P1–Re–P2, 175.6(1); N–Re–C1, 117.5(2); C1–Re–C7, 124.3(2).

$\text{O})_2]$ (Tc–C = 2.08–2.13 Å), the only technetium methyl complex structurally characterized to date,⁹ and in the binuclear carbonyl complex $[\text{Tc}_2(\mu\text{-H})(\mu\text{-NC}_5\text{H}_4)(\text{NC}_5\text{H}_5)_2(\text{CO})_6]$.¹⁰

The rhenium analogue $[\text{ReNPh}_2(\text{PPh}_3)_2]$ (**2**)¹¹ is isostructural to the technetium complex and depicts similar spectroscopic properties. **1** and **2** are surprisingly inert. Attempted reactions with PMe_2Ph , PMe_3 , and 1,2-dicyanoethene-1,2-dithiolate always resulted in the recovery of the starting complexes from the reaction solutions.

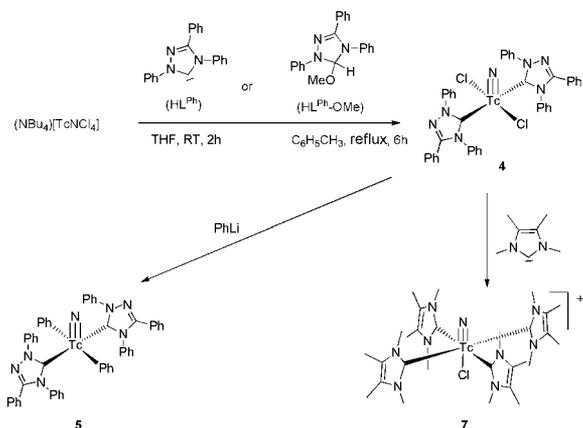
Unlike the situation with rhenium, where reactions of various nitridorhenium precursors with 1,3,4-triphenyl-1,2,4-triazol-5-ylidene (HL^{Ph}) always give $[\text{ReNCl}(\text{HL}^{\text{Ph}})(\text{L}^{\text{Ph}})]$ (**3**) with one orthometalated NHC ligand,¹² reactions of $(\text{NBu}_4)[\text{TcNCl}_4]$ with HL^{Ph} result in the formation of a five-coordinate

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technetium(V) compound having the composition $[\text{TcNCl}_2(\text{HL}^{\text{Ph}})_2]$ (**4**) (Scheme 2). Reduction of the metal in

Scheme 2. Syntheses and Reactions of Tc Triazolylidenes



such reactions is common, and in cases where the ligands are not reducing and no additional reducing agent is added, Cl^- ions may act as such. The two remaining chloro ligands of **4** can be substituted by phenyl ligands, resulting in the mixed aryl/carbene complex $[\text{TcNPh}_2(\text{HL}^{\text{Ph}})_2]$ (**5**).

The ^{13}C NMR spectra of the two complexes exhibit signals at 154.1 and 153.7 ppm, respectively, which can be assigned to the carbene carbon atoms. The spectrum of **5** contains an additional signal at 137.8 ppm corresponding to the phenyl carbon atoms bonded directly to the technetium atom. Crystal structure analysis of **5** (Figure 2) showed a five-coordinate

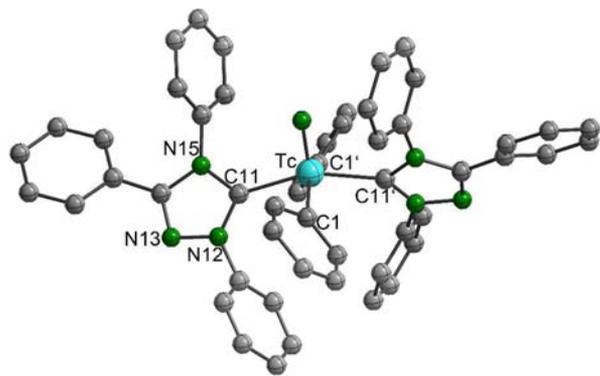
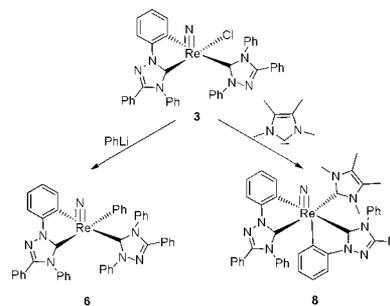


Figure 2. Molecular structure of **5**. H atoms and solvent molecules have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Tc–N, 1.606(4); Tc–Cl, 2.168(3); Tc–C11, 2.129(3); N–Tc–Cl, 104.5(1); N–Tc–C11, 101.2(1); C1–Tc–C11, 87.7(1); C1–Tc–C1', 157.6(2); C11–Tc–C11', 151.0(2).

complex with square-pyramidal geometry. Interestingly, the bonds of the technetium atom to the NHC ligands ($\text{Tc}-\text{C}_{\text{NHC}} = 2.129(3)$ Å) are slightly shorter than the bonds to the phenyl carbon atoms ($\text{Tc}-\text{C}_{\text{Ph}} = 2.168(3)$ Å).

The exclusively monodentate coordination of the triazolylidene ligands in the Tc complexes is in contrast to the coordination mode of triazolylidenes in the already known nitridorhenium complexes, which include one orthometalated ligand (e.g., **3** in Scheme 3). Orthometalation is not without precedent in the chemistry of HL^{Ph} but can hardly be predicted.¹³ It has been observed, for instance, in the ruthenium(II) complex $[\text{RuCl}_2(p\text{-cymene})(\text{HL}^{\text{Ph}})]$, which can

Scheme 3. Syntheses and Reactions of Re Triazolylidenes



be synthesized from $[\text{RuCl}_2(p\text{-cymene})]_2$.^{13a} In contrast, the benzylidene compound $[\text{RuCl}_2\{\text{P}(\text{C}_6\text{H}_{11})_3\}(\text{=CHPh})(\text{HL}^{\text{Ph}})]$ contains the carbene only as a monodentate ligand.¹⁴

Consequently, rhenium compound **3**, which was prepared following the procedure given in ref 12a, shows another reaction pattern with PhLi and forms the mixed aryl/carbene complex $[\text{ReNPh}(\text{HL}^{\text{Ph}})(\text{L}^{\text{Ph}})]$ (**6**). The ^{13}C NMR spectrum of **6** exhibits two carbene signals at 191.6 and 186.7 ppm as a result of the nonequivalence of the carbene carbon atoms. Two signals at 154.3 and 152.5 ppm correspond to the phenyl carbon atoms directly bonded to the rhenium atom. Similar chemical shifts were reported for **3**, with the signal of the carbene carbon atom trans to the chloro ligand shifted slightly downfield (200.1 ppm).^{12a} X-ray diffraction showed that the coordination mode in **6** is similar to those in the previously reported triazolylidene rhenium complexes $[\text{ReNX}(\text{HL}^{\text{Ph}})(\text{L}^{\text{Ph}})]$ (X = halide, pseudohalide, thiolate).¹² As in the case of the technetium complex **5**, two different metal–carbon bond lengths were observed, with the bonds to the carbene carbon atoms ($\text{Re}-\text{C}_{\text{NHC}} = 2.102(6)$ and $2.128(7)$ Å) being slightly shorter than the bonds to the phenyl carbon atoms ($\text{Re}-\text{C}_{\text{Ph}} = 2.160(7)$ and $2.169(7)$ Å) (Figure 3).

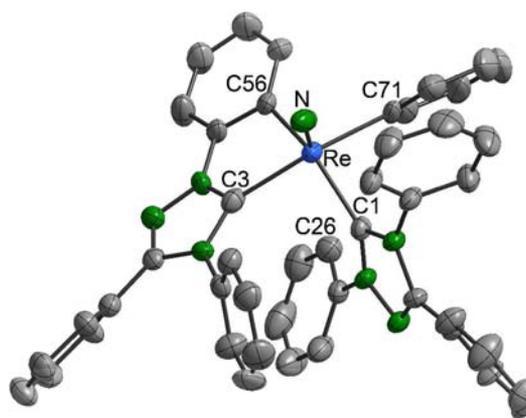


Figure 3. Molecular structure of **6**. H atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Re–N, 1.618(6); Re–C1, 2.102(6); Re–C3, 2.128(7); Re–C56, 2.169(7); Re–C71, 2.160(7); N–Re–C1, 102.4(3); C3–Re–C56, 75.4(3); C3–Re–C71, 150.1(3); C1–Re–C71, 89.3(3).

The different coordination modes of the triazolylidene ligands in rhenium complex **3** and technetium complex **4** result in different reactivities, as demonstrated by reactions with a more basic imidazolylidene. The technetium complex reacts with 1,3,4,5-tetramethylimidazol-2-ylidene (L^{Me}) via exchange of all of the equatorial ligands to form $[\text{TcNCl}(\text{L}^{\text{Me}})_4]\text{Cl}$ (**7**).

The product has an octahedral structure with the four NHC ligands arranged in a pinwheel-like fashion in the equatorial plane (Figure 4), a coordination mode that has been observed

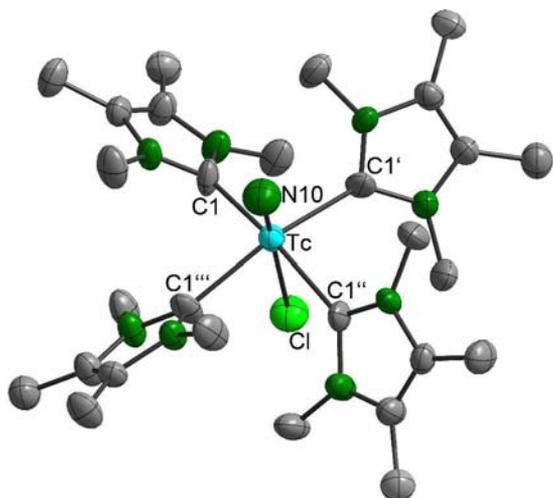


Figure 4. Molecular structure of **7**. H atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Tc–C1, 2.207(4); N–Tc–Cl, 180.0; C1–Tc–C1', 88.8(1).

previously for other technetium imidazolyliene complexes.⁵ The occupation of the axial coordination positions (i.e., the {N≡Tc–Cl}⁺ unit) is disordered along the fourfold axis of the tetragonal structure (space group *P4nc*). This required a refinement of the Cl and N atoms on shared positions, making the bond lengths on this axis less reliable. Details of the refinement model are given in the Supporting Information. Another type of disorder concerns the Cl[–] counterions, which are situated in channels formed by the large complex molecules on another fourfold axis parallel to the metal core. The Tc–C bond lengths are unexceptional with respect to other imidazolyliene technetium complexes.⁵

Treatment of **3** with L^{Me} in benzene results in the exclusive substitution of the chloro ligand and the formation of the first transition-metal complex containing imidazolyliene together with triazolyliene ligands. NMR or mass spectra of [ReN(L^{Me})(L^{Ph})₂] (**8**) could not be recorded because of the low solubility of **8** in inert solvents. In CDCl₃, in which the compound is readily soluble, it rapidly decomposes via formation of a paramagnetic species, most probably a Re^{IV} complex, which exhibits a broad EPR line at a *g* value of 2.031 without any hyperfine structure. Single crystals of **8** could be obtained by crystallization from a large amount of MeCN. Unfortunately, even the best data set obtained from our X-ray diffraction studies was of low quality (*R* value of 14.4%). Thus, the resulting bond lengths and angles are accordingly characterized by comparably large standard deviations and should not be overvalued. Only a structural sketch without ellipsoids is given in Figure 5. All of the main structural features of the compound, however, can certainly be derived from the structural analysis. The most interesting feature of **8** is the orthometalation of the second HL^{Ph} ligand (which was monodentate in **3**) trans to the nitrido ligand. Such a structural feature is without precedent and indirectly confirms the presence of agostic interactions in [ReNX(HL^{Ph})(L^{Ph})] complexes (X = halide, pseudohalide, thiolate), as recently postulated on the basis of crystal structure data.^{12b}

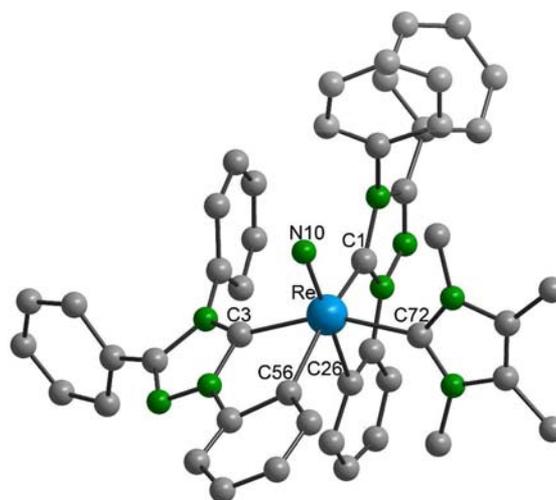


Figure 5. Molecular structure of **8**. H atoms have been omitted for clarity. Selected bond lengths (Å): Re–C1, 2.07(3); Re–C3, 2.15(4); Re–C72, 2.24(3); Re–C56, 2.19(3); Re–C26, 2.45(4).

In conclusion, previously unreported air-stable technetium complexes with phenyl and triazolyliene ligands have been synthesized, closing the last gap in the aryl chemistry of transition metals. Both the aryl and triazolyliene complexes show interesting reactivities and open new perspectives for the synthesis of stable organometallic technetium complexes. The chemistry of technetium with triazolylienes does not resemble that of rhenium, which should be subject of further studies.

■ ASSOCIATED CONTENT

📄 Supporting Information

Experimental procedures, characterization data, and crystallographic details for compounds **1**, **2**, **4**, **5**, **7**, and **8** (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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