Nitridotechnetium(V) Complexes with N-Heterocyclic Carbenes and Unexpected $(OSiMe_2OSiMe_2O)^{2-}$ Coligands

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Summary: Reactions of $[TcNCl_2(PPhR_2)_3]$ complexes (R = Me, Et) with 1,3-diethyl-4,5-dimethylimidazol-2-ylidene yield air-stable nitridotechnetium(V) complexes with N-heterocyclic carbenes with up to four of these bulky ligands and, depending on the reaction conditions applied, 1,1,3,3-tetramethyldisiloxane-1,3-diolato coligands which were abstracted from silicon-based grease.

N-Heterocyclic carbenes (NHC's) are known as strong Lewis bases and represent a promising alternative for phosphane ligands in coordination chemistry. There have only been a few reports about transition-metal or actinide complexes with NHC's that contain metals in high formal oxidation states,[1–7] and there exist only rare examples of complexes which have been studied by X-ray crystallography, such as a few oxo complexes of vanadium(V),[2a] titanium(IV),[6] uranium(VI),[7] and rhenium(V).[4,5] The recently reported dioxorhenium(V) complexes of the compositions $[ReO_2(HL^{i-Prop})_4]^+$ and $[ReO_2(L^R)_4]^+$ (HL^{i-Prop} = 1,3-diisopropylimidazol-2-ylidene and L^R = 1,3-dialkyl-4,5-dimethylimidazol-2-ylidenes, R = Me, Et, i-Prop) have remarkable stability and are
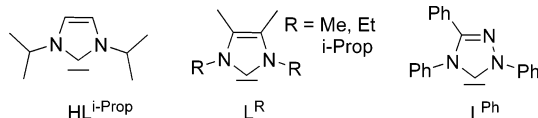
formed during reactions of the NHC's with various rhenium(V) precursors, which also include the nitrido complexes $[ReNCl_2(PPh_3)_2]$ and $[ReNCl_2(PMe_2Ph)_3]$.[4a] The unusual cleavage of a metal–nitrogen triple bond, and the formation of dioxo complexes and NH_3, was also observed during reactions of the analogous technetium nitrido complexes and L^{i-Prop}, which gave the hitherto only structurally characterized technetium complex with NHC ligands, $[TcO_2(L^{i-Prop})_4][TcO_4]$.[4a] The isolation of stable nitrido complexes with NHC's, to the best of our knowledge, has up to now succeeded only with the less nucleophilic triazol-5-ylidene derivative L^{Ph}. This NHC ligand can readily be generated by thermal methanol abstraction from 5-methoxy-1,3,4-triphenyltriazole and reacts with common nitridorhenium precursors under replacement of phosphane or halide ligands. Compounds with one or two such ligands have been reported recently.[8] Attempts to prepare analogous technetium complexes have failed up to now.

Stable nitridotechnetium(V) complexes with N-heterocyclic carbene ligands can be prepared from $[TcNCl_2(PR_2Ph)_3]$ complexes (R = Me, Et) and 1,3-diethyl-4,5-dimethylimidazol-2-ylidene (L^{Et}) when the reaction is performed under complete exclusion of air and moisture. Three different technetium-containing complexes were isolated, depending on the solvents and the reaction conditions applied.[9] They are the first

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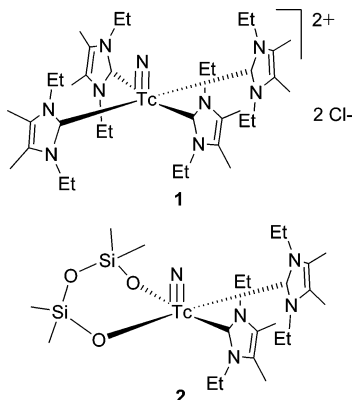
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(9) *Syntheses.* $[TcN(L^{Et})_4]Cl_2$ (**1**): $[TcNCl_2(PPhMe_2)_3]$ (60 mg, 0.1 mmol) was dissolved in 4 mL of dry THF. A solution of L^{Et} (76 mg, 0.5 mmol) in THF (2.5 mL) was added and the mixture stirred for 2 h. The color of the reaction mixture changed from yellow to red, and a yellow powder precipitated (47 mg, 59%). Dissolution in CH_3NO_2 and concentration yielded yellow-orange crystals. IR: $\nu_{Tc\equiv N}$ 1092 cm⁻¹ (m). ¹H NMR (CD₃CN; δ, ppm): CH_2 3.96 (m, 8H) and 4.52 (m, 8H), CH_3 (ethyl) 0.77 (tr, 12H) and 1.08 (tr, 12H), CH_3 (arom) 2.16 (s, 12H) and 2.17 (s, 12H). Anal. Calcd for $C_{36}H_{64}Cl_2N_9Tc$: Tc, 12.5. Found: Tc, 12.4. $[TcN(L^{Et})_2(OSiMe_2OSiMe_2O)]$ (**2**): concentration of the red mother liquor from the previous synthesis yielded orange-red crystals (about 20% yield). The same product was obtained by starting from $[TcNCl_2(PEt_2Ph)_3]$. The yield increases when a small amount of silicon grease is added directly to the THF solution. IR: $\nu_{Tc\equiv N}$ 1092 cm⁻¹ (m). ¹H NMR (CD₃CN, δ, ppm): CH_2 3.97 (m, 4H) and 4.12 (m, 4H), CH_3 (ethyl) 1.11 (tr, 12 H), CH_3 (arom) 2.14 (s, 12H), $SiCH_3$ −0.07 (s, 6H) and −0.09 (s, 6H). Anal. Calcd for $C_{22}H_{44}Si_2N_5O_3Tc$: Tc, 17.0. Found: Tc, 17.2. $[TcN(L^{Et})(PMe_2Ph)(OSiMe_2OSiMe_2O)]$ (**3**): $[TcNCl_2(PPhMe_2)_3]$ (60 mg, 0.1 mmol) was dissolved in 4 mL of dry acetonitrile. A solution of L^{Et} (76 mg, 0.5 mmol) in THF (2.5 mL) was added and the mixture stirred for 2 h. Red crystals deposited from the deep red solution upon concentration. IR: $\nu_{Tc\equiv N}$ 1084 cm⁻¹ (m). ¹H NMR (CDCl₃, δ, ppm): phenyl 7.2−8.6 (m, 5H), CH_2 2.83 (m, 1H), 3.34 (m, 1H), 3.68 (m, 1H), and 4.01 (m, 1H), CH_3 (ethyl) 1.15 (tr, 3H) and 1.20 (tr, 3H), CH_3 (arom) 2.05 (s, 3H) and 2.1 (s, 3H), $SiCH_3$ 0.03 (s, 3H), 0.04 (s, 3H), 0.09 (s, 3H), and 0.10 (s, 3H), CH_3 (phosphane) 1.64 (d, 3H) and 1.70 (d, 3H). ³¹P NMR (CDCl₃, δ, ppm): 17.5 (broad). Anal. Calcd for $C_{21}H_{39}Si_2N_3O_3PTc$: 17.5. Found: Tc, 17.5. *Crystal structure determinations*: CAD4 and Bruker Smart diffractometers, Mo Kα radiation, solution and refinement with SHELXS and SHELXL (G. M. Sheldrick, University of Göttingen, Göttingen, Germany). **1**: $C_{36}H_{64}Cl_2N_9Tc$, M_r = 791.87, monoclinic, $P2_1/n$, a = 11.498(2) Å, b = 28.649(5) Å, c = 14.131-(2) Å, β = 94.87(2)°, V = 4637(1) Å³, Z = 4, D_{calcd} = 1.134 g cm⁻³, θ = 3.06−26.00°, T = 293 K, 9012 reflections, μ = 0.459 mm⁻¹ (no absorption correction), 469 parameters, R1 = 0.0588, wR2 = 0.1611, GOF = 0.933. **2**: $C_{22}H_{44}N_5O_3Si_2Tc$, M_r = 580.80, monoclinic, $P2_1/n$, a = 10.057(2) Å, b = 18.112(3) Å, c = 15.597(3) Å, β = 95.44(1)°, V = 2828.2(9) Å³, Z = 4, D_{calcd} = 1.364 g cm⁻³, θ = 2.25−30.55°, T = 173 K, 8631 reflections, μ = 0.625 mm⁻¹ (no absorption correction), 298 parameters, R1 = 0.0296, wR2 = 0.0790, GOF = 1.071. **3**: $C_{21}H_{39}N_3O_3PSi_2Tc$, M_r = 566.70, monoclinic, $P2_1/n$, a = 9.294(2) Å, b = 35.556(7) Å, c = 9.554(1) Å, β = 115.40(1)°, V = 2852.0(9) Å³, Z = 4, D_{calcd} = 1.320 g cm⁻³, θ = 3.34−24.99°, T = 293 K, 4794 reflections, μ = 0.669 mm⁻¹ (no absorption correction), 280 parameters, R1 = 0.0602, wR2 = 0.1325, GOF = 0.863.

representatives of technetium nitrido complexes with NHC ligands.

A yellow solid of $[TcN(L^{Et})_4]Cl_2$ (**1**) precipitates from the reaction mixtures in medium yields (about 60% calculated for Tc) when THF is used as solvent. Con-

centration of the remaining dark red mother liquor and cooling results in the formation of a red, crystalline precipitate (about 20%). This product was identified as $[TcN(L^{Et})_2(OSiMe_2OSiMe_2O)]$ (**2**). The 1,1,3,3-tetramethyldisiloxane-1,3-diolato ligand is the result of serendipitous activation of silicon grease by the highly nucleophilic carbene. Similar reactions have been observed previously during the synthesis of a number of lanthanide and early-transition-metal complexes.[10] Very recently, there have also been reports about the formation of $(OSiMe_2OSiMe_2O)^{2-}$ ligands during reactions of gallium compounds with ^tBuAsLi and $[Ni(COD)_2]$ with an NHC.[11,12] In the chemistry of technetium and rhenium such reactions are without precedent. We undertook two experiments to confirm the nature and the origin of the chelating ligand in **2**, in addition to the crystallographic and spectroscopic data: (i) a reaction starting from $[TcNCl_2(PEt_2Ph)_3]$ to exclude that the {SiMe₂} fragment is a {PMe₂} building block derived from PMe₂Ph and (ii) addition of a drop of silicon grease directly to the solvent. The first reaction resulted in the same products that were obtained from $[TcNCl_2(PMe_2Ph)_3]$, and the latter gave a significantly higher yield of $[TcN(L^{Et})_2(OSiMe_2OSiMe_2O)]$ in comparison to that of $[TcN(L^{Et})_4]^{2+}$.

A ligand exchange intermediate of the formation of **2** can be isolated when the reaction is performed in acetonitrile. Deposition of **1** is prevented in this solvent, and a small amount (about 10%) of $[TcN(L^{Et})(PMe_2Ph)-(OSiMe_2OSiMe_2O)]$ (**3**) precipitates as orange-red blocks
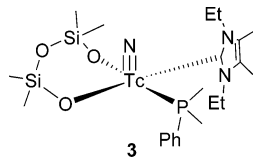
upon concentration. Further evaporation of the solvent gives **1**, but this product is contaminated with a number of side products, which favors its synthesis in THF.
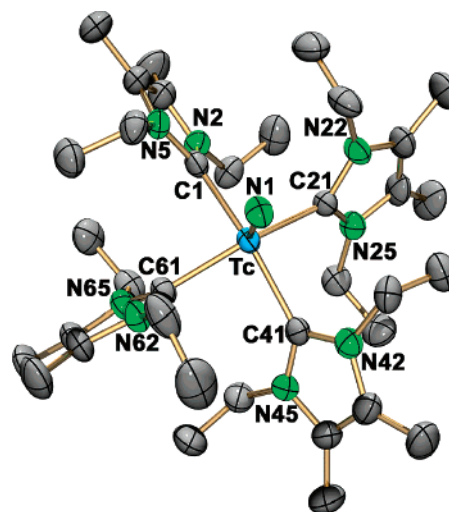

Figure 1. Structure of the complex cation in **1**. Selected bond lengths (Å) and angles (deg): Tc−N1 = 1.604(4), Tc−C1 = 2.192(5), Tc−C21 = 2.165(5), Tc−C41 = 2.191(5), Tc−C61 = 2.178(5); N1−Tc−C1 = 99.9(2), N1−Tc−C21 = 100.0(2), N1−Tc−C41 = 98.7(2), N1−Tc−C61 = 99.7(2). More bond lengths and angles are contained in Table S1 in the Supporting Information.

$[TcN(L^{Et})_4]Cl_2$ is soluble in acetonitrile and alcohols. It is stable in air as a solid; solutions, however, slowly decompose and an increasing amount of $[HL^{Et}]Cl$ can be detected in NMR spectra of the complex. The protons for its formation are derived from traces of water in the solvent. The IR spectrum of $[TcN(L^{Et})_4]Cl_2$ shows the $\nu_{Tc\equiv N}$ vibration at 1092 cm^{-1}. An X-ray structure analysis confirms that the technetium atom in the complex cation (Figure 1) is five-coordinate.[9] The basal plane of a distorted square pyramid is formed by the donor atoms of the four carbene ligands (maximum deviations from a least-squares plane: 0.009(2) Å, rms 0.0092), and the nitrido ligand forms its apex. The Tc atom is situated 0.363(2) Å above this plane. The four heterocyclic rings are arranged in a pinwheel-like fashion with torsion angles to the Tc−carbene plane between 56.9(2) and 66.0(2)°. This results in a highly shielded metal center (see also Figure S1 in the Supporting Information). The technetium−nitrogen distance of 1.604(4) Å is in the typical range for five-coordinate TcN complexes.[13] The long Tc−C bond lengths at or just under 2.2 Å are slightly longer than in the $[TcO_2(L^{i-Prop})_4]^+$ cation[4a] and indicate that the singlet carbenes function mainly as σ-donors. Although this conclusion cannot be drawn solely from a bond length consideration (also bearing in mind that the equatorial coordination sphere of the $[TcN(L^{Et})_4]^{2+}$ cation is sterically overcrowded), a technetium−carbon double bond with significant contributions from π back-bonding cannot plausibly be postulated for the electron-poor d^2 system. This is underlined by a comparison with the bonding situation in the Tc(I) carbene complexes $[Tc(=C=CHPh)Cl(DPPE)_2]$[14] and $[Tc(cp^*)(CO)_2(=CPhOEt)]$,[15] which belong to the vinylidene and Fischer

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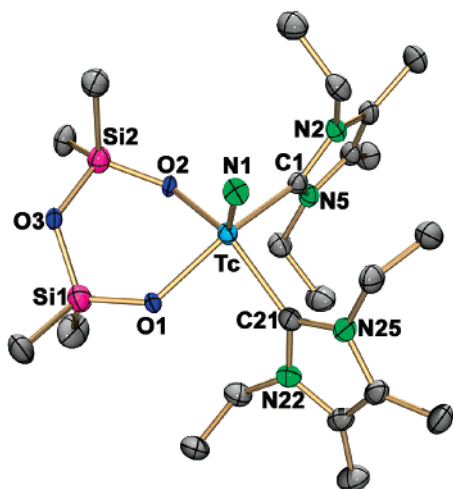
Figure 2. Ellipsoid representation of **2**. Selected bond lengths (Å) and angles (deg): Tc−N1 = 1.620(2), Tc−C1 = 2.127(2), Tc−C21 = 2.134(2), Tc−O1 = 2.060(1), Tc−O2 = 2.063(1), Si1−O1 = 1.605(1), Si1−O3 = 1.654(4), Si2−O2 = 1.608(1), Si2−O3 = 1.655(1); Tc−O1−Si1 = 131.62(8), O1−Si1−O3 = 111.09(7), O3−Si2−O2 = 101.31(7), Tc−O2−Si2 = 125.15(8), O1−Tc−O2 = 84.91(5). More bond lengths and angles are contained in Table S2 in the Supporting Information.

carbene types and show Tc−C bond lengths of 1.861 and 1.97 Å, respectively.

Two geometrically different ethyl and methyl groups can be derived from the ^{1}H NMR data of **1** (see also Figure S2 in the Supporting Information). More information about the suggested rotation barrier could not be derived in the accessible temperature range.

Compound **2** (Figure 2) is an air-stable solid that readily dissolves in chloroform or dichloromethane. The six-membered chelate ring is puckered, and the bond angles around the silicon atoms are close to the tetrahedral angle. A remarkable feature is the presence of two sets of Si−O bond lengths, which suggests some ionic character for the O3−Si bonds (cf. Si−O bonds of 1.631 Å in $(Me_3Si)_2O^{16}$ and 1.628 Å in $[(Me_2Si)O]_4{}^{17}$).

The bonding situation of the $(OSiMe_2OSiMe_2O)^{2-}$ ligand in **3** (Figure 3) is similar to that in **2**. A puckered six-membered chelate ring is formed, which contains two sets of Si−O bonds. The Tc−O bond lengths are slightly different with respect to the different ligands
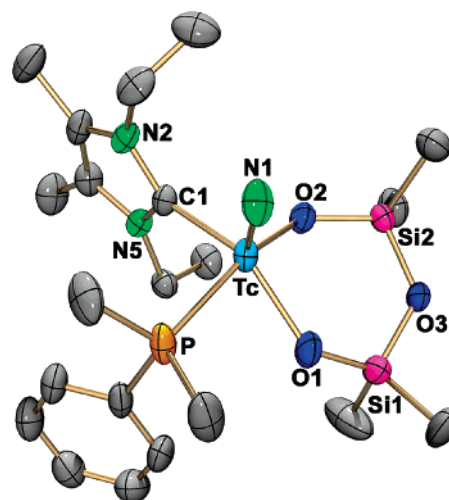

Figure 3. Molecular structure of **3**. Selected bond lengths (Å): Tc−N1 = 1.579(9), Tc−C1 = 2.071(9), Tc−P = 2.382-(3), Tc−O1 = 2.033(7), Tc−O2 = 2.053(6), Si1−O1 = 1.579-(7), Si1−O3 = 1.628(7), Si2−O2 = 1.584(6), Si2−O3 = 1.646(7). More bond lengths and angles are contained in Table S3 in the Supporting Information.

in trans positions. This suggests a structural trans influence for L^{Et}, which is somewhat less than that of PMe_2Ph.

The ^{1}H NMR spectra of **2** and **3** (Figures S3 and S6 in the Supporting Information) are complex and suggest rotational barriers in the Tc−C bonds. This behavior is not unexpected with respect to the presence of bulky ligands in the equatorial coordination spheres of the complexes (see also Figures S4 and S5 in the Supporting Information). Details on this rotational barrier are not available in the accessible temperature range.

The reproducible abstraction of 1,1,3,3-tetramethyl-disiloxane-1,3-diolato building blocks from silicon-based grease indicates the considerable synthetic potential of nucleophilic N-heterocyclic carbenes apart from their use as phosphane surrogates in coordination chemistry. The first overviews on this point have been published recently.[18] To avoid undesired side reactions on the coordination of $(OSiMe_2OSiMe_2O)^{2-}$ ligands to metal centers, silicon-free fittings must be used throughout all experimental procedures, including all previous operations such as drying of solvents.

Supporting Information Available: Figures and tables giving additional structural and spectroscopic data and CIF files giving crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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