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Note

The synthesis and structural characterization of the technetium nitrosyl complexes $[TcCl(NO)(SC_5H_4N)(PPh_3)_2]$ and $[Tc(NO)(SC_5H_4N)_2(PPh_3)]$

Terrence L. Nicholson [a,*], Ashfaq Mahmood [a], Peter Muller [b], Alan Davison [b], Shannon Storm-Blanchard [b], Alun G. Jones [a]

[a] Harvard Medical School, Department of Radiology, Boston, MA 02115, USA
[b] Massachusetts Institute of Technology, Department of Chemistry, Cambridge, MA 02139, USA

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ABSTRACT

The reaction of the Tc(I) complex $[Tc(NO)Cl_2(HOMe)(PPh_3)_2]$ with stoichiometric amounts of 2-mercaptopyridine and a proton scavenger yields $[Tc(NO)Cl(Spy)(PPh_3)_2]$ or $[Tc(NO)(Spy)_2(PPh_3)]$, depending upon quantities of ligands employed. These two complexes have been structurally characterized. The small bite angles of the bidentate mercaptopyridine ligands cause significant deviation from octahedral coordination geometry.

1. Introduction

The infrared spectra of nitrosyl complexes display strong, sharp absorptions in the 1550–1900 cm^{-1} region, and these absorptions are significantly influenced by the character of the ligands *trans*-to them [1]. This was displayed recently when comparing the IR spectra of the structurally characterized *mer*- and *fac*- isomers of $[TcCl_2(NO)(PNP_{pr})]$ [2].

The reaction of the Tc(II) nitrosyl complex $(Bu_4N)[TcNOCl_4]$ [3] with stoichiometric amounts of 2-mercaptopyridine (HSpy) and a proton scavenger gives a mixture of products as determined by multiple absorptions in this region in the infrared spectroscopy of the crude product. However, the reaction of $[TcCl_2(NO)(HOMe)(PPh_3)_2]$ with a stoichiometric amounts of 2-mercaptopyridine and a proton scavenger gives a single product, $[Tc(NO)Cl(PPh_3)_2(Spy)]$. The reaction with an excess of 2-mercaptopyridine and proton scavenger gives $[Tc(NO)(PPh_3)(Spy)_2]$.

2. Experimental

Caution! Technetium-99 is a weak β^--emitter ($E = 0.292$ MeV, $t_{1/2} = 2.12 \times 10^5$ years). All work has been done in laboratories approved for the use of low levels of radioactive materials. Precautions have been detailed elsewhere [4]. Reagents and solvents were used as received unless otherwise stated. Routine infrared spectra were obtained on a Perkin–Elmer Spectrum One FT-IR Spectrometer. Mass spectra were recorded on a Bruker Daltonics APEXII 3 Tesla Fourier Transform Mass Spectrometer (Ion Cyclotron Resonance Mass Spectrometer). See Table 1 for summation of X-ray crystallographic data set collection and refinement.

3. Synthesis

3.1. $[Tc(NO)Cl(Spy)(PPh_3)_2]$, complex (**1**)

To an orange solution of $[Tc(NO)Cl_2(HOCH_3)(PPh_3)_2]$ (79 mg, 0.104 mmol) and 2-mercaptopyridine (14 mg, 0.108 mmol) in dichloromethane was added diisopropylethylamine (27 mg, 0.209 mmol). This addition caused the solution to darken immediately to a wine red color. The sample was refluxed overnight, and no further color change was observed. The solution was concentrated to 1 ml under reduced pressure and then refrigerated overnight to yield a lilac-purple precipitate. The solid was collected on a fritted glass funnel, and dried in vacuo. Large, block shaped crystals of complex (**1**) formed overnight from dichloromethane layered with methanol and diethylether. Yield: 41 mg (50%).

Anal. Calc. for $C_{41}H_{34}ClN_2OP_2STc$: C, 61.65; H, 4.26; Cl, 4.39; S, 4.01. Found: C, 61.42; H, 4.30; Cl, 4.52; S, 4.11%.

FAB-MS(+): 798 $[Tc(NO)Cl(PPh_3)_2(Spy)]^+$, 763 $[Tc(NO)(PPh_3)_2(Spy)]^+$, 688 $[Tc(NO)Cl(PPh_3)_2]^+$, 536 $[Tc(NO)Cl(PPh_3)(Spy)]^+$, 501 $[Tc(NO)(PPh_3)(Spy)^+$. IR (KBr) (cm^{-1}): ν(NO) 1696 (vs, br).

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* Corresponding author.
E-mail address: terrence_nicholson@hms.harvard.edu (T.L. Nicholson).

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Table 1
Instrument employed – 'Siemens three-circle diffractometer, Bruker APEX CCD.

[TcCl(NO)(Spy)(PPh_3)$_2$]	[Tc(NO)(Spy)2(PPh_3)]	
Symmetry	monoclinic	monoclinic
Space group	*P*2(1)/m	*C*2/c
Cell length *a*	9.5620(14)	34.217(3)
Cell length *b*	24.715(4)	9.4819(8)
Cell length *c*	15.456(2)	16.3980(15)
Cell angle α	90.00	90.00
Cell angle β	90.006(2)	92.052(2)
Cell angle γ	90.00	90.00
Cell volume	3652.6(9)	5316.9(8)
Cell formula units *Z*	4	8
Temperature	100(2)	100.2
Reflections used	9851	9567
Theta minimum	2.47	2.38
Theta maximum	30.43	30.54
Crystal description	needle	plate
Crystal color	purple	red
Crystal size	0.30 × 0.12 × 0.07	0.45 × 0.30 × 0.05
Density calc	1.451	1.526
Absorption coefficient μ	0.648	0.768
T_{max}/T_{min}	0.9561/0.8294	0.9618/0.7188
SADABS (Sheldrick, 2009), total reflections collected	93,802	68,710
Theta maximum/minimum	29.57/1.32	29.57/1.19
R, R_w	0.0530/0.0863	0.0263/0.0619
Goodness-of-fit (GOF)	1.048	1.078

^{1}H NMR (CD_2Cl_2): 7.59 (m, 12H), 7.29 (m, 18H), 6.73 (m, 2H), 6.03 (d of d, 1H), 5.65 (t of d, 1H).

*3.2. [Tc(NO)(Spy)$_2$(PPh_3)], complex (**2**)*

A mixture of 2-mercatopyridine (10 mg, 0.09 mmol) and diisopropylethylamine (15 mg, 0.116 mmol) was added to a solution of [Tc(NO)Cl(Spy)(PPh_3)$_2$] (38 mg, 0.062 mmol) in dichloromethane. The orange solution rapidly darkened to a ruby red color within minutes. The ruby solution was refluxed for 24 h, after which time it was concentrated under reduced pressure. Slow evaporation at room temperature resulted in the formation of a deep orange microcrystalline solid. The product was collected on a fritted glass funnel and dried in vacuo and recrystallized from dichloromethane layered with methanol and ether. Yield: 12 mg (40%).

Anal. Calc. for $C_{28}H_{28}N_3OPS_2Tc$: C, 54.99; H, 3.76; N, 6.87; S, 10.47. Found: C, 54.88; H, 3.74; N, 6.82; S, 10.55%.

FAB-MS(+) (*m/z*): 611 [Tc(NO)(PPh_3)(Spy)$_2$]$^+$, 581 [Tc(PPh_3)(Spy)$_2$]$^+$, 501 [Tc(NO)(PPh_3)(Spy)]$^+$, 349 [Tc(NO(Spy)$_2$]$^+$, 319 [Tc(Spy)$_2$]$^+$.

IR (KBr) (cm^{-1}): ν(NO) 1677 (vs).

^{1}H NMR ((CD_3)$_2$CO): t $\sim$ 8.30 (d of d, 1H), 7.56 (m, 7H), 7.37 (m, 10H), 7.11 (t of d, 1H), 6.93 (d of d, 1H), 6.86 (m,1H), 6.51 (d of d, 1H), 6.22 (t of d, 1H).

4. Discussion

In exploring the coordination chemistry of technetium nitrosyl complexes with polydentate ligands, we have recently concluded that the Tc(II) precursor (Bu_4N)[$TcNOCl_4$] is too reactive to allow selective incorporation of polydentate ligands and formation of a single product. Reactions invariably lead to the formation of multiple products, which is easily observed in the infrared spectra of the crude products. Multiple absorptions in the 1550–1900 cm^{-1} region, where few other functional groups display absorption bands, is an easy and accurate method for monitoring how many products are present in a crude product. We recently reported multiple structural isomers of the Tc(I) complex [$TcCl_2$NO(PNP)], isolated and structurally characterized from the reaction of [$TcNOCl_4$]$^-$ and the neutral, tridentate ligand [2]. The redox active Tc(II) complex [$TcNOCl_4$]$^-$ can be easily reduced to Tc(I), which can lead to redox chemistry competing with the substitution reaction. Additionally, the labile chloride ligands, along with the coordinative unsaturation of this square pyramidal synthon, contribute to the lack of stereo selectivity in reactions with polydentate ligands. This has led us to explore alternative nitrosyl precursors, which are inherently less reactive and which allow a more selective incorporation of the polydentate ligands. The precursor we utilized in this study is [$TcCl_2$(NO)(HOMe)(PPh_3)$_2$], a Tc(I) species [6]. This complex appears ideal for this application in that it contains a combination of easily replaced hard and soft ligands allowing a more selective introduction of these polydentate ligands.

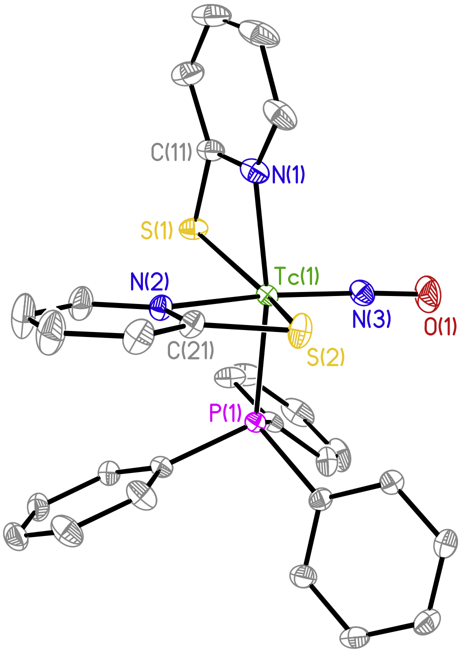

Fig. 1. ORTEP diagram of complex **2**, [Tc(NO)Cl(Spy)$_2$(PPh_3)].

Table 2
Selected bond lengths (Å) and angles (°) for [TcCl(NO)-(Spy)(PPh_3)$_2$].

Tc–Cl1	2.4410(11)
Tc–N2	1.748(4)
Tc–S1	2.4979(11)
Tc–N1	2.173(4)
Tc–P1	2.4338(8)
Tc–P2	2.4312(8)
N2–O1	1.196(5)
O1 N2 Tc1	177.7(3)
N2 Tc1 N1	167.63(15)
N2 Tc1 P1	90.36(2)
N1 Tc1 P1	89.995(19)
N2 Tc1 P1	90.36(2)
N1 Tc1 P1	89.995(19)
P1 Tc1 P1	176.70(4)
N2 Tc1 Cl1	103.86(11)
N1 Tc1 Cl1	88.52(10)
P1 Tc1 Cl1	88.348(19)
P1 Tc1 Cl1	88.348(19)
N2 Tc1 S1	101.81(11)
N1 Tc1 S1	65.82(10)
P1 Tc1 S1	91.505(18)
P1 Tc1 S1	91.505(18)
Cl1 Tc1 S1	154.33(4)

Table 3
Selected bond lengths (Å) and angles (°) for $[Tc(NO)(Spy)(PPh_3)]$.

Tc–N2	2.1771(12)
Tc–N3	1.7497(12)
Tc–N1	2.1527(13)
Tc–S1	2.4445(4)
Tc–S2	2.4676(4)
Tc–P1	2.3777(4)
N3–O1	1.1941(17)
O1 N3 Tc1	173.35(12)
N3 Tc1 N1	97.91(5)
N3 Tc1 N2	163.59(5)
N1 Tc1 N2	84.00(5)
N3 Tc1 P1	89.22(4)
N1 Tc1 P1	166.25(4)
N2 Tc1 P1	92.48(3)
N3 Tc1 S1	105.27(4)
N1 Tc1 S1	67.00(4)
N2 Tc1 S1	90.52(3)
P1 Tc1 S1	99.832(13)
N3 Tc1 S2	97.33(4)
N1 Tc1 S2	93.21(3)
N2 Tc1 S2	66.27(3)
P1 Tc1 S2	97.537(13)
S1 Tc1 S2	151.528(13)

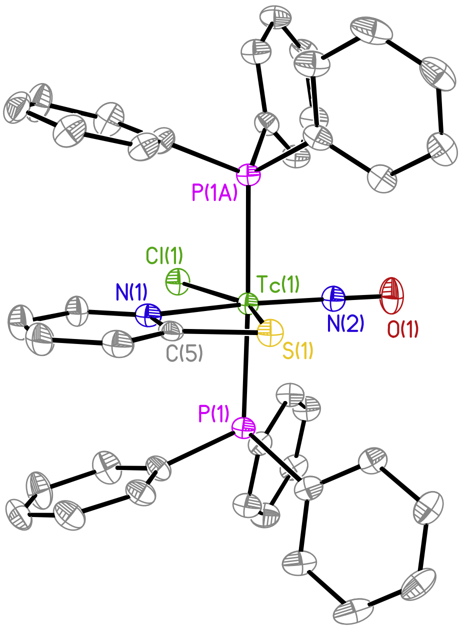

Fig. 2. ORTEP diagram of complex **1**, $[Tc(NO)Cl(Spy)(PPh_3)_2]$.

In the reactions with 2-mercaptopyridine and a proton scavenger, depending on the stoichiometries employed, the monosubstituted product $[TcClNO(Spy)(PPh_3)_2]$ or the disubstituted product $[TcNO(Spy)_2(PPh_3)]$ can be formed [7]. Both complexes have been previously reported synthesised from $[TcCl_2NO(NCMe)(PPh_3)_2]$ [5].

The X-ray crystal structure of $[TcClNO(Spy)(PPh_3)_2]$ displays the bulky triphenylphosphine ligands in mutually *trans*- coordination sites and the nitrosyl nitrogen *trans*- to the mercaptopyrindine nitrogen. An ORTEP diagram of $[TcClNO(Spy)(PPh_3)_2]$ is shown in Fig. 1, with selected bond lengths and angles in Table 2. The nitrosyl ligand is in linear form, with Tc–N–O bond angle at 177.7(3)° and short bond lengths of Tc–N 1.748(4) Å and N–O 1.196(5) Å, reflecting the multiple bonding throughout the unit. The small bite angle of the mercaptopyridine, N1–Tc–S1 is 65.82(10)°, results in significant distortion from octahedral around the equatorial band.

The X-ray crystal structure of $[TcNO(Spy)_2(PPh_3)]$ also displays the nitrosyl ligand in linear coordination mode with Tc–N–O bond angle of 173.35(12)° and short Tc–N and N–O bond lengths of 1.7497(12) Å and 1.1941(17) Å. The distortion in this *bis*-chelate complex from ideal octahedral coordination geometry is significant. A pyridine nitrogen is coordinated *trans*- to the phosphine with the P–Tc–N bond angle of 166.25(4)°. The two sulfur atoms are *trans*- to each other with the S–Tc–S bond angle of 151.528(13)°. Selected bond lengths and angle can be seen in Table 3. An ORTEP diagram of $[TcNO(Spy)_2(PPh_3)]$ is shown in Fig. 2.

5. Summary

By employing the less reactive, octahedral, Tc(I) nitrosyl precursor $[TcCl_2(NO)(HOMe)(PPh_3)_2]$ we were able to synthesize and easily isolate the *mono*-mercaptopyridine $[Tc(NO)Cl(Spy)(PPh_3)_2]$ and the *bis*-mercaptopyridine complex $[Tc(NO)(Spy)_2(PPh_3)]$ cleanly, and report the X-ray crystal structures of both. For a comprehensive discussion of the spectroscopy of these complexes see [5].

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2010.09.025.

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