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LETTER

Synthesis of $Tc(NO)(PPh_3)_3(H)_2$: a novel hydrido complex of technetium

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A number of nitrosyl complexes of technetium have been prepared [1–12]. These compounds contain nitric oxide as an NO^+ ligand and exist in a variety of oxidation states (I–III). The availability of the easily accessible starting materials, $[(C_4H_9)_4N][Tc(NO)Cl_4]$ [5–7] and $Tc(NO)(PPh_3)_2Cl_3$ [12], will allow further exploration of nitric oxide complexes of technetium. In this paper we describe the preparation and characterization of a novel diamagnetic dihydrido complex of technetium(I) containing a nitrosyl *trans* to a hydrido ligand.

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 [13, 14].

Syntheses

Ammonium pertechnetate was supplied as a gift from DuPont/Biomedical Products. Reagents and solvents were used as received unless otherwise indicated. The starting materials, $[(C_4H_9)_4N][Tc(NO)Cl_4]$ [5], $Tc(NO)(PMe_2Ph)_2Cl_3$ [11] and $Tc(NO(PPh_3)_2Cl_3$ [12] were prepared as described elsewhere. Routine ^1H NMR spectra were recorded on a Varian VXR-500 FTNMR spectrometer, routine IR spectra on a Mattson Cygnus 100 spectrophotometer. Fast atom bombardment mass spectra (FAB-MS(+) and FAB-MS(−)) were recorded with a MAT 731 mass spectrometer equipped with an Ion Tech B11N FAB gun or a custom-built Cs ion gun and operating at an accelerating voltage of +8 kV, or a JEOL HX110 mass spectrometer operating at ±10 kV and equipped with a JEOL FAB gun. The Ion Tech and JEOL FAB guns produced beams of 6–8 keV xenon neutrals and the Cs ion gun produced a beam of 6–8 keV cesium ions. The samples were dissolved in a 3-nitrobenzyl alcohol matrix. Elemental analyses were performed by Atlantic Microlab, Norcross, GA.

$Tc(NO)(PPh_3)_3(H)_2$

To a 50 ml flask was added 170.6 mg triphenylphosphine (0.65 mmol), 73.9 mg $Tc(NO)(PPh_3)_3Cl_3$ (0.10 mmol) and about 30 ml freshly opened absolute ethanol. To this slurry was added 17.3 mg sodium borohydride (0.46 mmol). The reaction commenced immediately and was heated to reflux for 20 min, at which time a bright yellow precipitate was observed. The volume was reduced to about 10 ml and the yellow product was isolated on a fritted glass funnel, washed with ethanol and dried *in vacuo*. Yield: 74.9 mg yellow solid, 86%.

IR (Kbr): $\nu(NO) = 1636$ cm^{-1}; $\nu(M\text{–}H) = 1733$, 1185 cm^{-1}. ^1H NMR ($C_6D_5CD_3$, −40 °C): δ −1.5 (br, 1H); −3.45 (sextet, 1H). ^{31}P NMR ($C_6D_5CD_3$, −40 °C, relative to PPh_3): δ 49 (br, 1P); 68 (br, 2P). FAB-MS(+): $m/z = 915$ $(Tc(NO)(PPh_3)_3)^+$; 653 $(Tc(NO)(PPh_3)_2)^+$; 623 $(Tc(PPh_3)_2)^+$; 391 $(Tc(NO)(PPh_3))^+$; 361 $(Tc(PPh_3))^+$.

This compound was also prepared in a similar manner but using 252.7 mg $[(C_4H_9)_4N][Tc(NO)Cl_4]$ (0.49 mmol), 106.3 mg sodium borohydride (2.8 mmol) and 1.3 g triphenylphosphine (5 mmol), and heating to reflux for 60 min. The product was spectroscopically identical to $Tc(NO)(PPh_3)_3(H)_2$, above. Yield: 279.9 mg yellow solid, 62%.

$Tc(NO)(PPh_3)_3(D)_2$

The deuterated complex was prepared by the reaction of 24.2 mg $Tc(NO)(PPh_3)_2Cl_3$ (0.03 mmol) and 18.3 mg sodium borodeuteride (0.44 mmol) in the presence of 150 mg triphenylphosphine (0.57 mmol) in about 3 ml methanol-d_4. The reaction was heated to reflux for 20 min before the yellow product was isolated on a fritted glass funnel, washed with deuterated methanol, and dried *in vacuo*. Yield: 24.3 mg yellow solid, 83%.

IR (KBr): $\nu(NO) = 1659$ cm^{-1}; $\nu(M\text{–}D) = 1358$, 801 cm^{-1}. FAB-MS(+): $m/z = 915$ $(Tc(NO)(PPh_3)_3)^+$; 653 $(Tc(NO)(PPh_3)_2)^+$; 623 $(Tc(PPh_3)_2)^+$; 361 $(Tc(PPh_3))^+$.

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The dideuteride was also prepared by the reaction of 137.1 mg $[(C_4H_9)_4N][Tc(NO)Cl_4]$ (0.27 mmol) with 79.4 mg sodium borodeuteride (1.89 mmol) in the presence of 766.2 mg triphenylphosphine (2.92 mmol) in about 4 ml methanol-d_4 and heating to reflux for 60 min. The yellow product was spectroscopically identical to $Tc(NO)(PPh_3)_3(D)_2$, above.

$Tc(NO)(PMe_2Ph)_2(PPh_3)(H)_2$

To a 25 ml round-bottom flask was added 33.75 mg $Tc(NO)(PMe_2Ph)_2Cl_3$, 224 mg triphenylphosphine, 28 mg sodium borohydride and about 15 ml absolute ethanol. The solution was heated to reflux. After 10 min, a yellow solid was evident. The volume was decreased by rotary evaporation and the yellow solid was isolated by filtration, washed with a minimum of cold ethanol and dried *in vacuo*. Yield: undetermined due to an excess of triphenylphosphine which was not removable without decomposition of the product.

IR (KBr): $\nu(NO) = 1637$ cm^{-1}. ^1H NMR ($C_6D_5CD_3$): δ −4.4 (br); −6.3 (br). ^{31}P NMR ($C_6D_5CD_3$, relative to PPh_3): δ 1 (b, 1P); 16 (br, 1P); 77 (br, 2P). FAB-MS(+): $m/z = 667$ $(Tc(NO)(PMe_2Ph)_2(PPh_3))^+$; 529 $(Tc(NO)(PMe_2Ph)_2(PPh_3))^+$.

Results and discussion

The diamagnetic complex, $Tc(NO)(PPh_3)_3(H)_2$, was prepared by the reaction of either $Tc(NO)(PPh_3)_2Cl_3$ or $[(C_4H_9)_4N][Tc(NO)Cl_4]$ with sodium borohydride in ethanol with an excess of triphenylphosphine.

The FAB-MS(+) mass spectrum of the product shows molecular fragments corresponding to the molecular ion with loss of the two hydrogen ligands ($m/z = 915$), followed by loss of one phosphine ($m/z = 653$), one phosphine and the nitrosyl ($m/z = 623$), two phosphines ($m/z = 391$), and two phosphines and the nitrosyl ligand ($m/z = 361$). The molecular ion itself is not observed, suggesting that the hydrogen ligands are labile. Evidence for the existence of the hydride ligands, while not available from the mass spectrum, is seen in the infrared and NMR spectra.

A comparison of the infrared spectrum of $Tc(NO)(PPh_3)_3(H)_2$ with the isotopically substituted dideuteride (Fig. 1) shows evidence for strongly coupled $\nu(Tc–H)$ and $\nu(TcNO)$ at 1733 and 1636 cm^{-1}, respectively. The strong absorption at 1185 cm^{-1} can be assigned to $\nu_{asym}(TcH)$ because it moves to 801 cm^{-1} on deuteration. The coupling is effectively removed from the nitrosyl because this absorption increases in energy and occurs at 1659 cm^{-1} in the dideuterio complex.

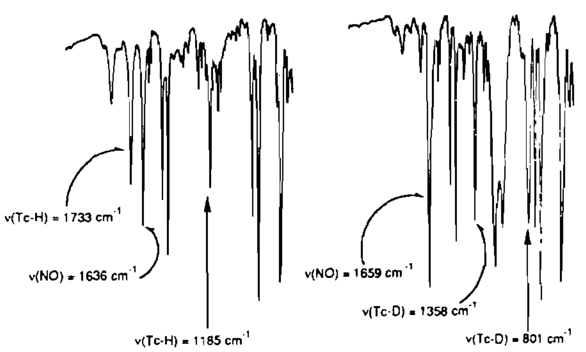

Fig. 1. Infrared spectra of $Tc(NO)(PPh_3)_3(H)_2$ and $Tc(NO)(PPh_3)_3(D)_2$.

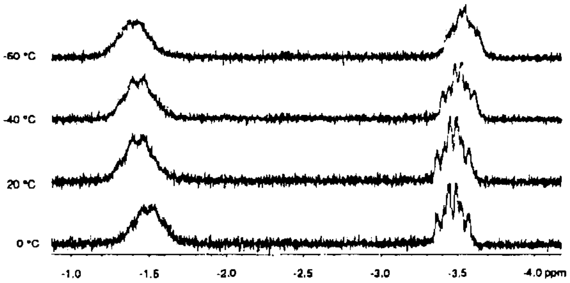

Fig. 2. ^1H NMR spectra of $Tc(NO)(PPh_3)_3(H)_2$.

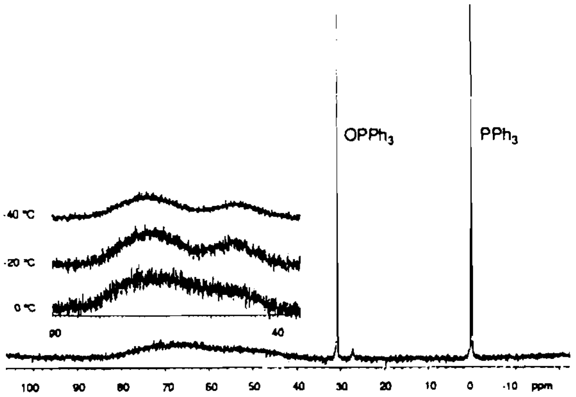

Fig. 3. ^{31}P spectra of $Tc(NO)(PPh_3)_3(H)_2$.

The ^1H NMR spectrum of this complex is somewhat complicated since the hydrides may be coupled to each other, to all three phosphorus nuclei, and to the technetium nucleus. The resonances are broadened into the baseline in the room temperature spectrum. However, cooling the sample effectively decouples the hydride from the quadrupolar technetium, and the two hydride resonances may be observed (Fig. 2). These resonances integrate in a ratio of one to one and the poorly resolved coupling to the phosphorus nuclei is visible in the upfield resonance. Coupling of the hydrides to each other is not observed. Viscosity broadening prevents further resolution of either resonance at lower temperatures.

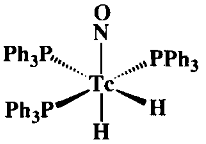

Fig. 4. Proposed geometry of $Tc(NO)(PPh_3)_3(H)_2$.

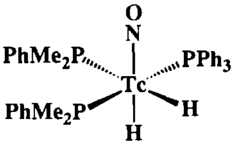

Fig. 5. Proposed geometry of $Tc(NO)(PMe_2Ph)_2(PPh_3)(H)_2$.

The ^{31}P NMR is also observable only at low temperature (Fig. 3). The spectrum is obtained with broad-band decoupling of the hydrides, and it is necessary to thermally decouple the technetium by lowering the temperature. Two broad resonances are resolved, one at 68 ppm and one at 47 ppm. These resonances integrate in a ratio of two to one, respectively. Therefore, the resonance at 68 ppm corresponds to the *trans*-phosphines and the one at 47 ppm corresponds to the phosphine *trans* to a hydride (Fig. 4).

Other dihydrides can be synthesized. For example, when $Tc(NO)(PMe_2Ph)_2Cl_3$ is reacted with sodium borohydride with an excess of triphenylphosphine, a yellow compound is obtained which exhibits two hydride resonances in the proton NMR spectrum at -4.4 and -6.3 ppm, integrating in a one to one ratio. There are three resonances in the ^{31}P NMR spectrum at 77, 16 and 1 ppm, which integrate in a ratio of one to one to one. In order for there to be three inequivalent phosphorus nuclei in the ^{31}P NMR spectrum, the two dimethylphenylphosphine ligands may not be mutually *trans*. This information leads to the formulation of the product as $Tc(NO)(PMe_2Ph)_2(PPh_3)(H)_2$, with the proposed structure shown in Fig. 5.

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