

ordination of the second metal ion by other donor groups present in the ligand. Binuclear coordination is probably also associated with redistribution of some of the donor groups associated with Cu(II) in the mononuclear complex, thus contributing to the lower formation constant for the second step. The 2:1 Cu(II) complex also undergoes two protonation reactions ( $\log K^H_{M_2HL} = 2.47$ ,  $\log K^H_{M_2H_2L} = 2.74$ ) and a series of four deprotonation reactions ( $\log K^{-H}_{M_2HL} = -3.07$ ,  $\log K^{-H}_{M_2LH_2} = -6.60$ ,  $\log K^{-H}_{M_2LH_3} = -7.97$ ,  $\log K^{-H}_{M_2LH_4} = -10.13$ ). The first three deprotonations probably involve the displacement of N-bound protons, in view of the implications made above that each Cu(II) in the binuclear complex is bound to one or two phenolate donors.

**Tripositive Metal Ions.** From the equilibrium constants shown in Table III, it is apparent that the trivalent ions form a group of their own and are therefore discussed together. The Fe(III) chelate is seen to have the highest stability constant, closely followed by Ga(III), In(III), and Al(III). Since the  $\log K_{ML}$  of Fe(III) (25.0) is much lower than that of HBED (39.8), it follows that the coordinate bonding of Fe(III) in the TGTC chelate may be similar to that of Cu(II) with two phenolate groups bound. However, there must be some structural differences, since the Fe(III) and Ga(III) chelates do not undergo protonation as readily as is the case with

Cu(II). Besides a weak one for Fe(III), a protonated chelate MHL was found for Al(III) and In(III) as well as for all the chelates of the divalent metal ions. At higher pH values, it seems that Fe(III) has greater affinity for phenolate donor groups, as is evidenced by the lower proton affinity of FeL ( $\log K = -4.54$ ) as compared to those of Ga(III), In(III), and Al(III). Since subsequent dissociation reactions show little discrimination between the trivalent metal ions, these reactions must also take place at remote sites such as the amino donor atoms.

It is unfortunate that stability constant information for metal complexes of other chelating ligands having a single phenolic group are almost nonexistent. Such data would be useful in sorting out the coordination possibilities with more complex ligands such as TGTC. In future studies by this group, the reactions of trivalent metal ions with sexadentate or highly polydentate ligands having only one phenolic donor group will be investigated.

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## Synthesis and Characterization of Hexakis(alkyl isocyanide) and Hexakis(aryl isocyanide) Complexes of Technetium(I)

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The complexes  $[Tc(CNR)_6]PF_6$  (where R = *tert*-butyl, methyl, cyclohexyl, and phenyl) have been prepared by reduction of the pertechnetate ion with aqueous  $Na_2S_2O_4$  in the presence of the isocyanide ligands. These complexes have been characterized by elemental analysis, optical, infrared, and  $^1H$  NMR spectroscopy, conductance, cyclic voltammetry, and field desorption mass spectrometry.

### Introduction

The widespread use of the metastable isotope of technetium ( $^{99m}Tc$ ) in diagnostic nuclear medicine procedures is well documented.<sup>1,2</sup> This, in part, is due to the favorable nuclear properties of this isotope ( $\gamma = 140$  keV,  $t_{1/2} = 6$  h) that allow  $\gamma$  camera images of high resolution to be obtained with a low-radiation dose to the patient. During the last 7 years, the use of macroscopic amounts of the readily available long-lived radionuclide  $^{99}Tc$ , a  $\beta$ -particle emitter ( $t_{1/2} = 2.12 \times 10^5$  years), has enabled substantial progress to be made in the basic chemistry of this element. Much of this work has been directed toward the investigation of kinetically inert complexes formed in oxidation states that are readily accessible in aqueous media by the reduction of the pertechnetate ion. These studies have demonstrated that it is possible to prepare classes of stable complexes in both the V and the III oxidation states with the appropriate choice of ligands.<sup>3,4</sup>

Recently, we reported the preparation of hexakis(*tert*-butyl isocyanide)technetium(I) hexafluorophosphate from the reaction of hexakis(thiourea-S)technetium(III) chloride with *tert*-butyl isocyanide in refluxing methanol.<sup>5</sup> We now report

the synthesis and characterization of this and related complexes by direct reduction of the pertechnetate ion in aqueous ethanol with sodium dithionite ( $Na_2S_2O_4$ ) in the presence of the isocyanide ligands.

This in turn has enabled us (a) to synthesize this class of air- and water-stable complexes at tracer concentrations (ca.  $10^{-8}$ – $10^{-9}$  M) with metastable  $^{99m}Tc$ , (b) to begin to evaluate the biological distributions of these complexes in animals, and (c) to establish structure-function correlations on a potentially large class of well-characterized complexes. We have demonstrated that certain members of this class have potential use in diagnostic nuclear medicine for lung perfusion studies, imaging of normal myocardial tissue, the detection of vascular

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emboli, and the labeling of cells, platelets, and liposomes.<sup>5-7</sup>

### Experimental Section

Technetium as  $\text{NH}_4^{99}\text{TcO}_4$  was obtained as a gift from New England Nuclear (NEN), Billerica, MA. All manipulations were carried out in laboratories approved for low-level radioactivity ( $^{99}\text{Tc}$  is a weak  $\beta$ -emitter with a half-life of  $2.12 \times 10^5$  years and particle energy of 0.292 MeV). All precautions followed have been detailed elsewhere.<sup>3</sup> Rhenium as  $\text{NaReO}_4$  was obtained from Cleveland Refractory Metals, Solon, OH.

Infrared spectra were recorded in the range 4000–300  $\text{cm}^{-1}$  on a Perkin-Elmer PE180 grating infrared spectrometer as Nujol mulls and as methylene chloride solutions. Optical spectra, in solution, were measured with a Cary 17 spectrophotometer. Conductivity measurements were performed in acetonitrile with use of a Yellow Springs Model 3403 conductivity cell and a Beckman RC-16C conductivity bridge.  $^1\text{H}$  NMR spectra were obtained from a Varian T-60 spectrometer with  $\text{Me}_4\text{Si}$  as the internal calibrant. Melting points were obtained with a Mel-Temp apparatus and are uncorrected. Voltammetric studies were carried out by using a PAR Model 174 polarographic analyzer with a stationary Pt electrode. All potentials were referenced to a saturated calomel electrode. Ferrocene was used as an internal calibrant. Tetra-*n*-butylammonium perchlorate was used as the supporting electrolyte, and Spectrograde acetonitrile was used as solvent. Field desorption mass spectra were measured with a Varian MAT 731 instrument described elsewhere.<sup>8</sup> Prior to use, distilled water was passed through a Barnstead Ultrapure D8902 cartridge, followed by redistillation in a Corning AG-1 water still. Cyclohexyl isocyanide was obtained from Strem Chemicals, Inc., while *tert*-butyl isocyanide, methyl isocyanide, and phenyl isocyanide were prepared by literature methods.<sup>9,10</sup>  $\text{Na}_2\text{S}_2\text{O}_4$  was a Fisher product.  $\text{ReOCl}_3(\text{PPh}_3)_2$  was prepared from  $\text{NaReO}_4$  by a literature method.<sup>11</sup> All other chemicals were used without further purification unless otherwise specified. Elemental analyses were performed by Atlantic Microlab, Inc., Atlanta, GA.

**Preparation of the Complexes. Hexakis(*tert*-butyl isocyanide)-technetium(I) Hexafluorophosphate.** To a 100 mL round-bottom flask were added a stir bar, ethanol (15 mL), water (15 mL, pH adjusted to 12 with NaOH), *tert*-butyl isocyanide (2 mL, 19.0 mmol), and 1.01 mL of 0.418 M  $\text{NH}_4\text{TcO}_4$  (0.42 mmol). The reaction mixture was heated to reflux on a heating mantle, and 0.20 g of  $\text{Na}_2\text{S}_2\text{O}_4$  (1.15 mmol) dissolved in pH 12 water (5 mL) was added dropwise over a 5-min period. Solutions of  $\text{Na}_2\text{S}_2\text{O}_4$  must be prepared immediately before use. After the solution was refluxed for 30 min, an additional 0.20 g of  $\text{Na}_2\text{S}_2\text{O}_4$  (1.15 mmol) in pH 12 water (5 mL) was added dropwise, and the solution was refluxed for 30 min. The colorless reaction mixture was transferred to a 100-mL beaker and the volume reduced by half by boiling off solvent on a hot plate. Water (40 mL) was added and the solution cooled to room temperature. A 0.50-g sample of  $\text{NH}_4\text{PF}_6$  in water (5 mL) was added, immediately precipitating a white solid. This material was collected by vacuum filtration, washed with water (10 mL) and ether (10 mL), and dried in vacuo. The complex was recrystallized by slow evaporation of an acetone-water (4:1 v/v) solution, yielding 0.30 g of white, crystalline  $[\text{Tc}(\text{CNC}(\text{CH}_3)_3)_6]\text{PF}_6$  (0.41 mmol), 98% based on Tc; mp >200 °C. The complex is soluble in polar organic solvents. Anal. Calcd for  $\text{C}_{30}\text{H}_{54}\text{F}_6\text{N}_6\text{PTc}$ : C, 48.50; H, 7.34; N, 11.32. Found: C, 48.48; H, 7.45; N, 11.31. Optical spectrum (acetonitrile): 235 nm ( $\epsilon$   $8.0 \times 10^4$  L mol<sup>-1</sup> cm<sup>-1</sup>), 260 (sh). IR (Nujol):  $\nu_{\text{CN}}$  2090 (s), 2045 (s) cm<sup>-1</sup>. IR (methylene chloride solution):  $\nu_{\text{CN}}$  2090 (s), 2060 (s) cm<sup>-1</sup>.  $^1\text{H}$  NMR (chloroform-*d*<sub>1</sub>): 1.50 (s) ppm. Conductivity (acetonitrile, 10<sup>-3</sup> M):  $\Delta_m = 140 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ . (+)FDMS:  $m/z$  597 (calcd for  $\text{C}_{30}\text{H}_{54}\text{N}_6\text{Tc}^+$  597).  $E_{1/2}$ (anodic) = 0.83 V vs. SCE (1 e, reversible).

**Hexakis(methyl isocyanide)technetium(I) Hexafluorophosphate.** This complex was prepared similarly to  $[\text{Tc}(\text{CNC}(\text{CH}_3)_3)_6]\text{PF}_6$  in 96% yield by using methyl isocyanide instead of *tert*-butyl isocyanide; mp >200 °C dec. Anal. Calcd for  $\text{C}_{12}\text{H}_{18}\text{F}_6\text{N}_6\text{PTc}$ : C, 29.39; H, 3.71; N, 17.14. Found: C, 29.50; H, 3.72; N, 17.07. Optical spectrum (acetonitrile): 263 nm ( $\epsilon$   $4.1 \times 10^4$ ), 229 ( $7.3 \times 10^4$ ). IR (Nujol):  $\nu_{\text{CN}}$  2110 (s) cm<sup>-1</sup>. IR (methylene chloride solution):  $\nu_{\text{CN}}$  2130 (s) cm<sup>-1</sup>.  $^1\text{H}$  NMR (acetonitrile-*d*<sub>3</sub>/dimethyl-*d*<sub>6</sub> sulfoxide (4:1 v/v)): 2.95 (s) ppm. Conductivity (acetonitrile, 10<sup>-3</sup> M):  $\Delta_m = 135 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ . (+)FDMS:  $m/z$  345 (calcd for  $\text{C}_{12}\text{H}_{18}\text{N}_6\text{Tc}^+$  345).  $E_{1/2}$ (anodic) = 0.82 V vs. SCE (1 e, reversible).

**Hexakis(phenyl isocyanide)technetium(I) Hexafluorophosphate.** This complex was prepared as pale yellow crystals in 32% yield by a method similar to that used for  $[\text{Tc}(\text{CNC}(\text{CH}_3)_3)_6]\text{PF}_6$ . The complex was recrystallized by chilling (-15 °C) an acetonitrile/ether (3:1 v/v) solution; mp >200 °C. Anal. Calcd for  $\text{C}_{42}\text{H}_{30}\text{F}_6\text{N}_6\text{PTc}$ : C, 58.47; H, 3.51; N, 9.74. Found: C, 58.30; H, 3.68; N, 9.67. Optical spectrum (acetonitrile): 355 nm (sh), 295 ( $7.5 \times 10^4$ ), 230 (sh), 223 ( $7.8 \times 10^4$ ). IR (Nujol):  $\nu_{\text{CN}}$  2070 (s), 1980 (sh) cm<sup>-1</sup>. IR (methylene chloride solution):  $\nu_{\text{CN}}$  2085 (s) cm<sup>-1</sup>.  $^1\text{H}$  NMR (chloroform-*d*<sub>1</sub>): 7.50 (s) ppm. Conductivity (acetonitrile, 10<sup>-3</sup> M):  $\Delta_m = 130 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ . (+)FDMS:  $m/z$  717 (calcd for  $\text{C}_{42}\text{H}_{30}\text{N}_6\text{Tc}^+$  717).  $E_{1/2}$ (anodic) = 1.18 V vs. SCE (1 e, reversible).

**Hexakis(cyclohexyl isocyanide)technetium(I) Hexafluorophosphate.** This material was prepared similarly to  $[\text{Tc}(\text{CNC}(\text{CH}_3)_3)_6]\text{PF}_6$  in 45% yield. However, the complex was isolated in a different manner. After refluxing, the reaction mixture was transferred to a 100-mL beaker and 0.5 g of  $\text{NH}_4\text{PF}_6$  in water (5 mL) was added. The volume of the solution was reduced by half with use of a hot plate, and water (40 mL) was added. The solution was cooled to room temperature and was extracted with ether (2 × 15 mL). To the ether phase was added hexane (100 mL), precipitating an off-white solid. This material was redissolved in ether (25 mL) and precipitated with hexane (100 mL). Two recrystallizations by slow evaporation of an acetone/water (4:1 v/v) mixture yielded white, crystalline  $[\text{Tc}(\text{CNC}_6\text{H}_{11})_6]\text{PF}_6$ , mp 129 °C. Anal. Calcd for  $\text{C}_{42}\text{H}_{66}\text{F}_6\text{N}_6\text{PTc}$ : C, 56.10; H, 7.40; N, 9.35. Found: C, 56.28; H, 7.51; N, 9.35. Optical spectrum (acetonitrile): 263 nm ( $\epsilon$   $4.1 \times 10^4$ ), 233 ( $7.0 \times 10^4$ ). IR (Nujol):  $\nu_{\text{CN}}$  2080 (s), 2040 (sh) cm<sup>-1</sup>. IR (methylene chloride solution):  $\nu_{\text{CN}}$  2090 (s) cm<sup>-1</sup>.  $^1\text{H}$  NMR (chloroform-*d*<sub>1</sub>): 1.7 (br), 3.8 (br) ppm. Conductivity (acetonitrile, 10<sup>-3</sup> M):  $\Delta_m = 131 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ . (+)FDMS:  $m/z$  753 (calcd for  $\text{C}_{42}\text{H}_{66}\text{N}_6\text{Tc}^+$  753).  $E_{1/2}$ (anodic) = 0.88 V vs. SCE (1 e, reversible).

**Hexakis(*tert*-butyl isocyanide)rhenium(I) Hexafluorophosphate.** To a 100-mL round-bottom flask were added a stirbar, 0.20 g of  $\text{ReOCl}_3(\text{PPh}_3)_2$  (0.24 mmol), methanol (30 mL), *tert*-butyl isocyanide (3 mL, 28.5 mmol), and water (30 mL, pH adjusted to 12 with NaOH). After this slurry was heated to reflux, 0.50 g of solid  $\text{Na}_2\text{S}_2\text{O}_4$  (2.87 mmol) was slowly added to the reaction mixture. Over the next 48 h, an additional 0.30 g of  $\text{Na}_2\text{S}_2\text{O}_4$  (1.72 mmol) was added to the refluxing solution at approximately 12-h intervals. The reaction mixture was then transferred to a 100-mL beaker and its volume reduced by half on a hot plate. Water (40 mL) was added to the solution, which, when cooled to room temperature, was filtered through Celite. To this colorless, clear solution was added 0.50 g of  $\text{NH}_4\text{PF}_6$  in water (5 mL), immediately precipitating a white solid. This material was collected by suction filtration, washed with water (10 mL) and ether (10 mL), and dried in vacuo. Recrystallization by slow evaporation of an acetone/water (4:1 v/v) solution yielded 0.10 g of white, crystalline  $[\text{Re}(\text{CNC}(\text{CH}_3)_3)_6]\text{PF}_6$  (0.12 mmol), 50% based on Re; mp >200 °C. Anal. Calcd for  $\text{C}_{30}\text{H}_{54}\text{F}_6\text{N}_6\text{PRe}$ : C, 43.42; H, 6.56; N, 10.13. Found: C, 43.25; H, 6.57; N, 10.02. Optical spectrum (acetonitrile): 260 nm (sh), 230 ( $9.7 \times 10^4$ ). IR (Nujol):  $\nu_{\text{CN}}$  2100 (s), 2060 (s) cm<sup>-1</sup>.  $^1\text{H}$  NMR (methylene-*d*<sub>2</sub> chloride): 1.50 (s) ppm. Conductivity (acetonitrile, 10<sup>-3</sup> M):  $\Delta_m = 140 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ . (+)FDMS:  $m/z$  683, 685 (due to the two Re isotopes,  $^{185}\text{Re}$  and  $^{187}\text{Re}$ ) (calcd for  $\text{C}_{30}\text{H}_{54}\text{N}_6\text{Re}^+$  683, 685).  $E_{1/2}$ (anodic) = 0.74 V vs. SCE (1 e, reversible). The  $^1\text{H}$  NMR, IR, and voltammetric data are in agreement with the data reported by Walton et al.<sup>12</sup>

**Attempted Reaction of  $[\text{Tc}(\text{CNH}_3)_6]\text{PF}_6$  with Methylamine.** In a 50-mL round-bottom flask were mixed 0.05 g of  $[\text{Tc}(\text{CNH}_3)_6]\text{PF}_6$  (0.10 mmol), methanol (30 mL), and aqueous 40% methylamine (1 mL). This mixture was refluxed for 2 h. At this time, the reaction

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mixture was transferred to a 100-mL beaker, water (20 mL) was added, and the methanol was allowed to evaporate. White crystals of starting material (as identified by IR) were quantitatively recovered.

### Results and Discussion

The reaction of the pertechnetate ion with  $\text{Na}_2\text{S}_2\text{O}_4$  in ethanolic aqueous base in the presence of an excess of RNC (where R = methyl, *tert*-butyl, cyclohexyl, and phenyl) produces the technetium(I) cations,  $[\text{Tc}(\text{CNR})_6]^+$ , in fair to excellent yields.<sup>13</sup> These complexes have been isolated as their hexafluorophosphate salts and have been characterized by elemental analysis, IR, optical, and  $^1\text{H}$  NMR spectroscopy, conductance, cyclic voltammetry, and field desorption mass spectrometry.

The  $[\text{Tc}(\text{CNR})_6]\text{PF}_6$  species are air and water stable, are soluble in polar organic solvents, and are 1:1 electrolytes in acetonitrile solution.<sup>14</sup> The complexes of the alkyl isocyanides are white, crystalline solids while the phenyl isocyanide complex is pale yellow. This color difference has been observed in the manganese and rhenium analogues and is due to the tailing of the 295-nm absorption band in  $[\text{Tc}(\text{CNPh})_6]^+$  into the visible spectrum.<sup>15,16</sup> All of the complexes exhibit intense metal to ligand charge-transfer bands in their optical spectra.<sup>17</sup>

In the infrared spectra of all the  $[\text{Tc}(\text{CNR})_6]\text{PF}_6$  complexes, there are intense absorptions between 2130 and 2040  $\text{cm}^{-1}$  due to the  $\text{C}\equiv\text{N}$  stretching modes. For all of these complexes the  $\nu_{\text{CN}}$  in ca. 50–80  $\text{cm}^{-1}$  lower in energy than the band in the uncomplexed ligand, consistent with extensive  $\pi$ -donation from the Tc(I) core to the isocyanide ligands.

The mull spectra of the complexes show splitting of the CN mode for R =  $\text{C}_6\text{H}_5$ ,  $\text{C}_6\text{H}_{11}$ , and *t*- $\text{C}_4\text{H}_9$ . In methylene chloride solution the *tert*-butyl complex exhibits prominent bands at 2090 and 2060  $\text{cm}^{-1}$ , but the others show only a single band. This splitting of the  $\nu_{\text{CN}}$  band has been observed in solution spectra of the rhenium *tert*-butyl analogue and also in other isoelectronic hexakis(isocyanide) complexes.<sup>12,17,18</sup>

The complexes cannot have  $\text{O}_h$  symmetry. The highest symmetry possible for R =  $\text{CH}_3$  and *t*- $\text{C}_4\text{H}_9$  is  $S_6$  for which two bands ( $A_u$  and  $E_u$ ) are expected. The phenyl complex on the other hand could have  $T_h$  symmetry for which only one CN stretch ( $T_u$ ) is expected. The phenyl complex may have  $S_6$  or lower symmetry in the solid state, but the symmetry is probably  $T_h$  in solution. The single peak in the methyl complex must arise from the accidental degeneracy of the CN stretching modes. Presumably the relatively small methyl group has little effect on the energies of the  $A_u$  and  $E_u$  modes, and the complex appears to have virtual  $\text{O}_h$  symmetry. Clearly, in the case of the *tert*-butyl complex, steric interactions of the bulky *t*- $\text{C}_4\text{H}_9$  groups lead to a discernible energy separation between the CN modes. The two-band pattern in the infrared spectrum can be accommodated by a number of geometrical structures. The most symmetrical ( $S_6$ ) would be expected to minimize interligand repulsive forces.

Voltammetric studies in acetonitrile of the  $[\text{Tc}(\text{CNR})_6]\text{PF}_6$  (R = alkyl) complexes reveal a reversible one-electron oxidation at 0.82–0.88 V vs. SCE.<sup>19</sup>  $[\text{Tc}(\text{CNPh})_6]\text{PF}_6$  is

somewhat harder to oxidize, exhibiting a reversible one-electron oxidation at 1.18 V vs. SCE. This trend, also observed for the  $\text{Mn}(\text{CNR})_6^+$  analogues, is due to the greater electron-withdrawing capability of aryl isocyanides.<sup>20</sup> The Re(I) complex  $[\text{Re}(\text{CNC}(\text{CH}_3)_3)_6]\text{PF}_6$  exhibits a reversible one-electron oxidation at 0.74 V vs. SCE, 90 mV less positive than that of the Tc analogue. This is consistent with the observed trend that technetium complexes are harder to oxidize than their rhenium analogues.<sup>21</sup>

We have previously shown that field desorption mass spectrometry (FDMS) can be used to characterize Werner-type coordination compounds that are involatile salts.<sup>8</sup> Simple spectra resulted from these anionic technetium complexes in both the negative ((-)FDMS) and positive ((+)FDMS) ion modes.<sup>22,23</sup> For the compounds described here, the strong signals associated with the cations  $[\text{Tc}(\text{CNR})_6]^+$  are the only features found in the (+)FD mass spectra. This makes their interpretation both facile and unambiguous. Although the manganese(I) and rhenium(I) hexakis(isocyanide) cations have been known for some years, they are not prepared by the reduction of the oxyanions ( $[\text{MnO}_4]^-$ ,  $[\text{ReO}_4]^-$ ) in aqueous solution.<sup>12,16,24</sup> Thus, the facile synthesis of the technetium complexes from  $[\text{TcO}_4]^-$  under mild conditions is both novel and intriguing.

Unlike pertechnetate, perrhenate is not reduced by  $\text{Na}_2\text{S}_2\text{O}_4$  in aqueous base, even under reflux. However, when  $\text{ReOCl}_3(\text{PPh}_3)_2$  is reduced under these conditions in the presence of *tert*-butyl isocyanide,  $[\text{Re}(\text{CNC}(\text{CH}_3)_3)_6]^+$  can be isolated as its hexafluorophosphate salt in 50% yield. These kinetically inert, low-spin  $d^6$  cations differ from their isoelectronic ruthenium analogues. For example,  $[\text{Tc}(\text{CNC}-\text{H}_3)_6]\text{PF}_6$  does not react with excess aqueous methylamine in refluxing methanol whereas under milder conditions  $[\text{Ru}(\text{CN}-\text{CH}_3)_6][\text{PF}_6]_2$  readily forms diaminocarbene complexes with this amine.<sup>25</sup> Apparently the lower charge on the technetium complex renders it less susceptible than the doubly charged ruthenium complex to nucleophilic attack by methylamine.

### Conclusion

Over the last few years, stable complexes of technetium in a variety of oxidation states have been prepared directly from pertechnetate in aqueous solution. As a reducing agent,  $\text{Na}_2\text{S}_2\text{O}_4$  has proven to be quite versatile in this context. Complexes of Tc(V) (e.g.,  $[\text{trans-TcO}_2(\text{cyclam})]^+$  and  $[\text{TcO}(\text{edt})_2]^-$ ) and Tc(III) (e.g.,  $\text{Tc}(\text{acac})_3$ ) have been prepared by the direct reduction of the pertechnetate ion with  $\text{Na}_2\text{S}_2\text{O}_4$  in the presence of the appropriate ligand.<sup>5,26,27</sup> As we have shown, even Tc(I), a relatively unexplored oxidation state, is accessible from pertechnetate in aqueous solution.

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**Registry No.**  $[\text{Tc}(\text{CNC}(\text{CH}_3)_3)_6]\text{PF}_6$ , 86767-65-9;  $[\text{Tc}(\text{CNC}-\text{H}_3)_6]\text{PF}_6$ , 86767-67-1;  $[\text{Tc}(\text{CNPh})_6]\text{PF}_6$ , 86767-69-3;  $[\text{Tc}(\text{CNC}-\text{H}_{11})_6]\text{PF}_6$ , 86767-71-7;  $[\text{Re}(\text{CNC}(\text{CH}_3)_3)_6]\text{PF}_6$ , 81625-51-6;  $\text{NH}_4\text{-TcO}_4$ , 13598-66-8;  $\text{ReOCl}_3(\text{PPh}_3)_2$ , 17442-18-1.

- (13) Recently, the isopropyl, *n*-propyl, and *n*-butyl analogues have been prepared in our laboratory and characterized by elemental analysis, IR spectroscopy, and field desorption mass spectrometry.  
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