CH_3, C_2H_5, C_6H_5).[14,15,35] Synthetic routes to these complexes usually start either with low-valent chlorides (which may be reduced by alkali-metal amalgams in the presence of phosphite) or with metal carbonyls that are activated thermally or photochemically to substitution by phosphite.

In this communication, we report the synthesis and characterization of the first binary technetium phosphite complex, $Tc[P(OCH_3)_3]_6^+$. This is the first ionic phosphite complex to be characterized from group 7B. The $Re[P(OCH_3)_3]_6^+$ species that was postulated has not yet been described.[2] In addition, we have prepared the complex by the direct reduction of $NaTcO_4$ with $P(OCH_3)_3$, an unprecedented reduction from M(VII) to M(I) in a single, fast, and simple reaction to give the phosphite complex. Finally, the title complex, a cationic technetium complex, is of interest in nuclear medicine, similar to other recently characterized cationic complexes.[36-38]

Synthesis of $Tc[P(OCH_3)_3]_6^+$ is readily accomplished in an inert atmosphere by adding excess $P(OCH_3)_3$ to a methanolic solution of $NaTcO_4$ (200:1 millimolar ratio), sealing the mixture in a pressure bottle (0.2 L), and heating at 100 °C for 0.5 h. Although the best yields are obtained by using freshly distilled $P(OCH_3)_3$ and dried methanol, substantial amounts of the complex form when reagents of lower purity are used. The reaction was not attempted in the presence of air or water because of the sensitivity of $P(OCH_3)_3$ to these substances. The ease with which the reduction from Tc(VII) to Tc(I) is accomplished is remarkable and demonstrates the powerful reductive action of $P(OCH_3)_3$ on oxo species. Reduction of sodium pertechnetate to the monovalent complex can be achieved in neat $P(OCH_3)_3$ and in tetrahydrofuran solutions of the ligand, demonstrating that $P(OCH_3)_3$ alone can be considered the reducing agent. Although methanol may also be involved in the reduction, its presence is not essential to the reaction. Other procedures leading to Tc(I) complexes either start with lower oxidation states, produce isolable intermediates, or use auxiliary reducing agents. For example, preparation of the $Tc(CNR)_6^+$ complexes[38] uses TcO_4^- as starting material with dithionite as reducing agent, and in the dmpe (dmpe = 1,2-bis(dimethylphosphino)ethane) series,[36,37] $TcO_2(dmpe)_2^+$ and $Tc(dmpe)_2Cl_2^+$ can be isolated as intermediates in the formation of $Tc(dmpe)_3^+$, which appears only after prolonged reaction. Although the initial $TcO_4^-/P(OCH_3)_3$ solution is red and may contain a complex of the intermediate oxidation state, reduction to the Tc(I) compound proceeds even at room temperature.

Isolation of the $Tc[P(OCH_3)_3]_6^+$ cation is based on the low solubility of the tetraphenylborate salt in methanol. Thus, when an argon-saturated solution of $NaB(C_6H_5)_4$ in methanol (1 M) is added to the cooled reaction mixture, a white precipitate forms immediately. The precipitate can be collected by filtration using Schlenk techniques and recrystallized from methanol. Typical yields range from 50 to 75%, but a second and third crop of crystals can be grown by evaporation of the mother liquor, substantially increasing the yield. Depending on the rate at which the white-colorless crystals form, either needles (fast) or plates (slow) are obtained. The crystals are stable in air for at least 6 months. Elemental analyses on the crystalline material are consistent with the formulation $Tc[P(OCH_3)_3]_6B(C_6H_5)_4$.

Nuclear magnetic resonance spectra of $Tc[P(OCH_3)_3]_6^+$ were obtained for ^{99}Tc ($I = {}^9/_2$) and ^{31}P ($I = {}^1/_2$) in deuterated chloroform and methanol, respectively. The ^{99}Tc spectrum contains the expected septet centered at −422 ppm vs. TcO_4^- with a Tc–P coupling constant of 909 Hz. This coupling constant with technetium is much larger than those observed previously for oxygen, fluorine, or hydrogen[39] and implies a large Tc–P interaction. The ^{31}P spectrum contains a decet centered at −158.5 ppm vs. 85% H_3PO_4 with a P–Tc coupling constant of 909 Hz. This chemical shift is well within the range observed for other metal phosphite complexes.[31,34] The ^{31}P spectrum clearly shows the nuclear Overhauser enhancement of the outermost peaks, whose intensity is noticeably larger than that of the eight inner peaks. The NMR spectra are readily interpreted as arising from an octahedral TcP_6 moiety containing six electronically equivalent phosphorus nuclei.

Mass spectra of $Tc[P(OCH_3)_3]_6B(C_6H_5)_4$ were obtained by fast atom bombardment mass spectrometry. In the positive-ion mode, the parent peak is at *m/e* 843 (calcd 843.4). Peaks at *m/e* 719, 595, and 471 correspond to loss of one, two, and three ligands from the parent ion. The peaks at *m/e* 719 and 595 are of approximately equal intensity and are the base peaks of the spectrum. Successive loss of CH_2 fragments is suggested by peaks occurring at *m/e* 829, 815, and 801 as well as *m/e* 705, 691, and 677. In the negative-ion mode, the parent peak is observed at *m/e* 319 (calcd 319.2).

Infrared spectra of $Tc[P(OCH_3)_3]_6B(C_6H_5)_4$ were taken from a pressed KBr pellet. The vibrational frequencies due to the P–O bonds shifted to higher energy in the complex (1011 to 1048 and 726 to 762 cm^{-1}), indicating that the $P(OCH_3)_3$ was coordinated to Tc. Bands to due $B(C_6H_5)_4^-$ were virtually unchanged from those of $NaB(C_6H_5)_4$, as expected for ionic tetraphenylborate.

In addition to the bands expected from $P(OCH_3)_3$ and $B(C_6H_5)_4^-$, an additional strong band that appeared at 538 cm^{-1} was tentatively assigned to a Tc–P vibration. Although a weak band does appear at 511 cm^{-1} in uncomplexed $P(OCH_3)_3$, the intensity of the band at 538 cm^{-1} suggests that it may include the Tc–P band since the relative intensities of all other $P(OCH_3)_3$ bands are unchanged from the uncomplexed ligand while this band greatly increases in intensity. However, in view of the fact that Tc–Cl stretching frequencies in $Tc(diars)_2Cl_2^+$ (diars = 1,2-bis(diphenylarsino)ethane) occur near 330 cm^{-1} and those for $Tc(dmpe)Cl_2^+$ are at nearly the same energy,[40] confirmation of the assignment of the Tc–P band must await infrared characterization of more members of this class of compounds.

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Isolation and Characterization of a Molybdenum-Containing Product in a Hydrazine-Forming Reaction[1]

Sir:

The isolation of $MoBr_3$(triphos), where triphos = $PhP(CH_2CH_2PPh_2)_2$, from the ammonia-forming reaction of an-

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hydrous HBr with *trans*-$[\mathrm{Mo(N_2)_2(triphos)(PPh_3)}]$ (**1**) in tetrahydrofuran (THF) solution was important in establishing the stoichiometry of the reaction (1), particularly since the

$$2\,trans\text{-}\underset{\mathbf{1}}{[\mathrm{Mo(N_2)_2(triphos)(PPh_3)}]} \xrightarrow[\text{THF}]{\text{HBr}} 2\mathrm{NH_4Br} + 3\mathrm{N_2} + 2\mathrm{MoBr_3(triphos)} + 2\mathrm{PPh_3} \quad (1)$$

nitrogen balance was usually low.[2,3] A similar reaction carried out in benzene solution produced both ammonia and hydrazine.[5] In both of these reactions it has been shown that at an early stage in the reaction a pair of isomeric hydrazido(2−) $\{\mathrm{Mo(NNH_2)}\}^+$ complexes were formed.[5] In THF solution a molybdenum(III) complex, $\mathrm{MoBr_3(triphos)}$, was the product in the ammonia-forming reaction (2). In benzene solution

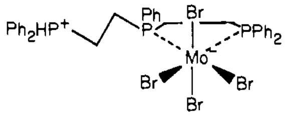
$$2\{\mathrm{Mo(NNH_2)}\}^+ \xrightarrow{\mathrm{H^+}} 2\mathrm{NH_4}^+ + \mathrm{N_2} + 2\{\mathrm{Mo(III)}\} \quad (2)$$

the four-electron reduction of dinitrogen to hydrazine could lead to a molybdenum(II) complex (eq 3) by analogy with the

$$2\{\mathrm{Mo(NNH_2)}\}^+ \xrightarrow{\mathrm{H^+}} \mathrm{N_2H_5}^+ + \mathrm{N_2} + 2\{\mathrm{Mo(II)}\} \quad (3)$$

$$\{\mathrm{Mo(NNH_2)}\}^+ \xrightarrow{\mathrm{H^+}} \mathrm{N_2H_5}^+ + \{\mathrm{Mo(IV)}\} \quad (4)$$

ammonia-forming reaction (2) or a molybdenum(IV) complex (eq 4). Careful workup of the reaction mixture in benzene after 60 h led to the isolation and characterization of a *single* molybdenum(III)-containing product, $[\mathrm{Mo^{-}Br_4(Ph_2PCH_2CH_2PPhCH_2CH_2PHPh_2{}^{+})}]$ (**2**).



In a typical reaction, benzene (20 mL) and HBr (20 mol/mol of Mo) were condensed onto a sample of **1** (ca. 0.2 mmol) at −196 °C. The mixture was allowed to warm to room temperature and stirred (ca. 60 h). Volatiles were removed from the suspension, and $\mathrm{CH_2Cl_2}$ (20 mL) was added. If ammonia and hydrazine were to be determined quantitatively, the mixture was stirred in vacuo for ca. 18 h before an aqueous extraction was carried out. On the other hand, in order to isolate the molybenum-containing product the mixture was filtered immediately after addition of $\mathrm{CH_2Cl_2}$ and the orange solution taken through three freeze–pump–thaw cycles before being allowed to stand at room temperature. Orange crystals of **2** began to form after about 1 h and were filtered off after 48 h, washed with $\mathrm{CH_2Cl_2}$, and dried in vacuo.[6] The formulation of **2** as a molybdenum(III) complex coordinated with four bromide ions and triphos behaving as a bidentate ligand, the third phosphorus atom being protonated, is based upon (i) the elemental analysis,[6] (ii) the presence of a ν(P–H) at 2350 cm^{-1}, and (iii) $\mu_{\mathrm{eff}} = 4.00\ \mu_{\mathrm{B}}$ (3.12 unpaired electrons) (Evans method[7]). Complex **2** was insoluble in all solvents that we tried. However, the addition of triethylamine to a suspension of **2** in $\mathrm{CH_2Cl_2}$ rapidly produced a clear orange solution. The magnetic susceptibility measurement was made on this solution. Complex **2** was recovered by adding HBr to the solution (eq 5).

$$\mathbf{2} \underset{\mathrm{HBr}}{\overset{\mathrm{NEt_3}}{\rightleftharpoons}} [\mathrm{MoBr_4(Ph_2PCH_2CH_2PPhCH_2CH_2PPh_2)}]^- + [\mathrm{NEt_3H}]^+ \quad (5)$$

Since ammonia was also a product in the reaction, a second molybdenum-containing product, $\mathrm{MoBr_3(triphos)}$, should be present. However, in separate experiments we have shown that $\mathrm{MoCl_3(triphos)}$ reacted with HX (X = Cl, Br) in $\mathrm{CH_2Cl_2}$ to produce a monoprotonated bidentate triphos complex, $[\mathrm{Mo^{-}Cl_4(Ph_2PCH_2CH_2PPhCH_2CH_2PHPh_2{}^{+})}]$, analogous to **2**. In fact the opening of one of the chelate rings of coordinated triphos caused by strong acid seems general for the types of complexes studied by us. For example, HCl reacted with $\mathrm{MoCl_2(triphos)(PPh_3)}$ in $\mathrm{CH_2Cl_2}$ to produce $[\mathrm{MoCl_4(Ph_2PCH_2CH_2PPhCH_2CH_2PHPh_2)}][\mathrm{HCl_2}]$. Therefore, it seems likely that any $\mathrm{MoBr_3(triphos)}$ formed in the reaction in benzene would be converted to **2** in the presence of HBr (which was present in excess).

The presence of only one molybdenum-containing product suggests one of two possibilities: (i) A single reaction pathway led to the formation of both ammonia and hydrazine (e.g., disproportionation) and one metal-containing product. (ii) Ammonia and hydrazine were formed in two separate reactions, but coincidently the isolated metal-containing product from each reaction was the same. We believe that the latter is the case and suggest that the molybdenum-containing product initially formed after hydrazine formation was either (i) a molybdenum(II) complex that was oxidized by HBr to **2**, (ii) a molybdenum(IV) hydride that reacted with $\mathrm{CH_2Cl_2}$ to lose H· and form **2**,[8] or (iii) a molybdenum(IV) complex that was reduced to **2**. Efforts are under way to identify the precursor to **2**.

The facile opening of one of the chelate rings of the tridentate ligand triphos in the presence of strong acid poses the question of the role that metal–triphos phosphorus bond cleavage may play during the reduction of coordinated dinitrogen in these systems.

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