

METAL-METAL MULTIPLY BONDED COMPLEXES OF TECHNETIUM

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**Metal-Metal Multiply Bonded Complexes of Technetium:
Los Alamos National Laboratory Final Technical Report
Research Foundation Project # RF-8347
March 30, 1995**

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Abstract

$\text{Tc}_2\text{Cl}_4(\text{PMe}_2\text{Ph})_4$ was readily oxidized by $[\text{Cp}_2\text{Fe}]^+$ to form the $\text{Tc}_2^{\text{II,III}}$ species $[\text{Tc}_2\text{Cl}_4(\text{PMe}_2\text{Ph})_4][\text{PF}_6]$. The relatively high positive potential of the second oxidation process precluded isolation of the quadruply bonded technetium species $[\text{Tc}_2\text{Cl}_4(\text{PR}_3)_4]^{2+}$. Oxidation of $\text{Tc}_2\text{Cl}_4(\text{PR}_3)_4$ in the presence of Cl^- resulted in substitution of one of the phosphine ligands in favor of a Cl^- to give the neutral $\text{Tc}_2^{\text{II,III}}$ species $\text{Tc}_2\text{Cl}_5(\text{PMe}_2\text{Ph})_3$. Electrochemical studies of $\text{Tc}_2\text{Cl}_5(\text{PMe}_2\text{Ph})_3$ indicated substitution of one phosphine ligand for a chloride makes formation of the quadruply bonded species more favorable. Further structural and spectroscopic characterization have been performed on the formamidinate complexes $\text{Tc}_2(\text{DTolF})_3\text{Cl}_2$ and $\text{Tc}_2(\text{DPhF})_4\text{Cl}$. The synthetic methodology for the preparation of these species was extended to dirhenium. This allowed for the isolation of the quadruply bonded dirhenium complex $\text{Re}_2(\text{DTolF})_3\text{Cl}_3$. $\text{Tc}_2\text{Cl}_4(\text{PR}_3)_4$ undergoes phosphine substitution reactions with the diphosphines dppe and dppm. Reaction of $\text{Tc}_2\text{Cl}_4(\text{PMe}_2\text{Ph})_4$ with excess dppe gave the bridged complex $\beta\text{-Tc}_2\text{Cl}_4(\text{dppe})_2$. While reaction with $\text{Tc}_2\text{Cl}_4(\text{PMePh}_2)_4$ produces the chelating isomer $\alpha\text{-Tc}_2\text{Cl}_4(\text{dppe})_2$ exclusively. The fully solvated complex $[\text{Tc}_2(\text{CH}_3\text{CN})_8]^{4+}$ was structurally characterized as the mixed triflate, tetrafluoroborate salt $[\text{Tc}_2(\text{CH}_3\text{CN})_8(\text{O}_3\text{SCF}_3)_2][\text{BF}_4]_2$. While $[\text{Tc}_2(\text{CH}_3\text{CN})_{10}][\text{BF}_4]_4$ is stable under thermal conditions, the Tc-Tc triple bond is cleaved photochemically to produce the mononuclear high-spin species $[\text{Tc}(\text{CH}_3\text{CN})_6][\text{BF}_4]_2$. The photochemistry of $[\text{Tc}_2(\text{CH}_3\text{CN})_{10}][\text{BF}_4]_4$ was investigated under a variety of conditions. Chemical reduction of $[\text{Tc}_2(\text{CH}_3\text{CN})_{10}][\text{BF}_4]_4$ produced the mixed valent complex $\text{Tc}_2(\mu, \eta^2\text{-CH}_3\text{CN})(\text{CH}_3\text{CN})_{10}[\text{BF}_4]_3$. Further spectroscopic data is reported for this unusual species. While $\text{Tc}_2(\mu, \eta^2\text{-CH}_3\text{CN})(\text{CH}_3\text{CN})_{10}[\text{BF}_4]_3$ exhibits a reversible oxidation couple in its cyclic voltammogram, chemical oxidation results in break-up of the bridging $\eta^2\text{-CH}_3\text{CN}$ linkage and formation of the mononuclear species $[\text{Tc}(\text{CH}_3\text{CN})_6]^{2+}$.

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Introduction

The primary objective of this project was to explore and develop the area of technetium metal-metal multiple bond chemistry. At the outset of the project, examples of metal-metal multiply bonded complexes of technetium were primarily limited to those supported by halide and carboxylate ligands. As a result, we intended to significantly expand the number of complexes containing Tc-Tc multiple bonds using ligands other than carboxylates or halides. In order to achieve this goal, the results obtained from years of dirhenium research was used as a guide for the development of new technetium compounds. Our emphasis, however, was on pursuing unanticipated results and exploiting the inherent differences between technetium and rhenium in order to develop chemistry beyond that which exists for rhenium. We have focused our attention on the preparation of dinuclear complexes with ligand sets that are known to support dinuclear metal-metal bonded cores in a variety of different metal oxidation states. Investigation of the consequences of electron addition and removal from metal-metal bonding manifold on the structural and physical properties of such dinuclear species will provide vital information regarding the electronic structure of Tc-Tc multiply bonded compounds.

Our earlier work had established a high yield synthetic route to the preparation of $\text{Tc}_2\text{Cl}_4(\text{PR}_3)_4$ $\text{PR}_3 = \text{PEt}_3, \text{P}(\text{n-Pr})_3, \text{PMe}_2\text{Ph}$ and PMePh_2 . These species represented the first discrete ditechneium complexes with an electron-rich triple bond. The triethylphosphine derivative, $\text{Tc}_2\text{Cl}_4(\text{PEt}_3)_4$, was exploited as a precursor to three new metal-metal bonded ditechneium compounds. Treatment of $\text{Tc}_2\text{Cl}_4(\text{PEt}_3)_4$ with $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ in acetonitrile yielded the fully solvated ditechneium cation $[\text{Tc}_2(\text{CH}_3\text{CN})_{10}]^{4+}$. Additionally, reaction of $\text{Tc}_2\text{Cl}_4(\text{PEt}_3)_4$ with *N,N'*-di-phenylformamidine (HDPHF) resulted in formation of tris- and tetra-bridged formamidinate complexes with concomitant oxidation of the di-metal centers to give $\text{Tc}_2(\text{DPhF})_3\text{Cl}_2$ and $\text{Tc}_2(\text{DPhF})_4\text{Cl}$. We have now expanded the focus of our research to include the chemistry of these new species. Furthermore, as part of an effort to prepare a series of complexes supported by an identical ligand set with varying bond order, we have examined the redox chemistry of $\text{Tc}_2\text{Cl}_4(\text{PMe}_2\text{Ph})_4$. Herein, we also report the investigation of the redox and photochemistry of the solvated dinuclear species $[\text{Tc}_2(\text{CH}_3\text{CN})_{10}][\text{BF}_4]_4$. Additional characterization of the formamidinate complexes $\text{Tc}_2(\text{DTolF})_3\text{Cl}_2$ and $\text{Tc}_2(\text{DPhF})_4\text{Cl}$ is included together with an extension of the synthetic methodology used for the preparation of the analogous dirhenium systems.

Oxidation Reactions of $\text{Tc}_2\text{Cl}_4(\text{PMe}_2\text{Ph})_4$

Previous electrochemical studies demonstrated that $\text{Tc}_2\text{Cl}_4(\text{PMe}_2\text{Ph})_4$ possesses two reversible one electron-oxidation processes. The first process is quite accessible occurring at $E_{1/2} = -0.26$ vs. ferrocene but the second oxidation, which occurs at $E_{1/2} = 0.92$, is much less chemically accessible. As anticipated, the triply bonded species $\text{Tc}_2\text{Cl}_4(\text{PMe}_2\text{Ph})_4$ is readily oxidized by one-electron using $[\text{Cp}_2\text{Fe}]^+$ as an oxidant to yield the mixed valent species $[\text{Tc}_2\text{Cl}_4(\text{PMe}_2\text{Ph})_4][\text{PF}_6]$. Slow addition of $[\text{Cp}_2\text{Fe}][\text{PF}_6]$ to a stirred solution of $\text{Tc}_2\text{Cl}_4(\text{PMe}_2\text{Ph})_4$ in acetonitrile yields a dark green solution from which $[\text{Tc}_2\text{Cl}_4(\text{PMe}_2\text{Ph})_4][\text{PF}_6]$ is isolated in nearly 80% yield. A cyclic voltammogram of the green crystalline product reveals two reversible one-electron redox couples at the same potential as those observed for the neutral species $\text{Tc}_2\text{Cl}_4(\text{PMe}_2\text{Ph})_4$. However, instead of these couples corresponding to two one-electron oxidation processes, these redox couples now correspond to a one electron oxidation and a one electron reduction, respectively. The similarity of the cyclic voltammograms of $[\text{Tc}_2\text{Cl}_4(\text{PMe}_2\text{Ph})_4]^+$ and $\text{Tc}_2\text{Cl}_4(\text{PMe}_2\text{Ph})_4$ indicate that no structural rearrangement has occurred upon oxidation and the metal-metal bond has remained intact. The electronic spectrum of $[\text{Tc}_2\text{Cl}_4(\text{PMe}_2\text{Ph})_4]^+$ exhibits a strong absorption in the near-IR at 1418 nm, characteristic of a M_2^{5+} core possessing a $\sigma^2\pi^4\delta^2\delta^{*1}$ ground-state electronic configuration. The band is assigned to an allowed $\delta \rightarrow \delta^*$ transition that was unavailable prior to removal of one electron from the δ^* orbital. X-ray crystallographic studies show that the molecule adopts an eclipsed M_2L_8 geometry similar to that observed for the neutral complex $\text{Tc}_2\text{Cl}_4(\text{PMe}_2\text{Ph})_4$. The Tc-Tc bond distance of 2.1062(8) Å is 0.03 Å shorter than that of $\text{Tc}_2\text{Cl}_4(\text{PMe}_2\text{Ph})_4$ consistent with the depopulation of a δ^* orbital which results in an increase in formal bond-order from 3 to 3.5. Similar bond distance changes were observed upon oxidation of the analogous $\text{Re}_2\text{Cl}_4(\text{PR}_3)_4$ type complexes. Unlike the structure of $\text{Tc}_2\text{Cl}_4(\text{PMe}_2\text{Ph})_4$, only one orientation of the Tc-Tc bond is observed. Presumably, the presence of the $[\text{PF}_6]^-$ anion helps orient the metal-metal core in a single direction.

While removal of one electron from $\text{Tc}_2\text{Cl}_4(\text{PMe}_2\text{Ph})_4$ can be readily achieved chemically, the high positive potential of the second oxidation process necessitates the use of a much stronger oxidizing agent. For this purpose, we selected the radical cation salt $[(p\text{-BrC}_6\text{H}_4)_3\text{N}][\text{SbCl}_6]$, which undergoes a reversible one electron reduction process near that of the second oxidation process of $\text{Tc}_2\text{Cl}_4(\text{PMe}_2\text{Ph})_4$ ($E_{1/2} = + 0.7$ V vs. ferrocene in CH_2Cl_2). Addition of two equivalents of $[(p\text{-BrC}_6\text{H}_4)_3\text{N}][\text{SbCl}_6]$ to a stirred acetonitrile solution of $\text{Tc}_2\text{Cl}_4(\text{PMe}_2\text{Ph})_4$ resulted in the gradual formation of green product that was admixed with a yellow-orange species. Surprisingly, the green product was found to be soluble in toluene identifying it as a neutral species. Slow evaporation of the toluene solution yielded a small crop of blue-green crystals. The product was identified by X-ray crystallography as the unusual extended chain complex $\text{TcCl}_4(\text{PMe}_2\text{Ph})_2 \cdot 2\text{SbCl}_3$. The solid state structure consists of individual $\text{TcCl}_4(\text{PMe}_2\text{Ph})_2$

moieties weakly interacting through the 4 Cl atoms with one SbCl_3 molecule on either side of $\text{TcCl}_4(\text{PMe}_2\text{Ph})_2$. The Sb -- Cl distances are rather long at 3.207(2) Å and 3.471(2) Å. In contrast, the terminal Sb-Cl distances are much shorter at 2.387(2) Å. In addition to the interaction with the Cl atoms of $\text{TcCl}_4(\text{PMe}_2\text{Ph})_2$, the Sb center is also closely associated with 2 adjacent carbon atoms of the phenyl ring with Sb-C distances of 3.49(1) Å and 3.51(1) Å. The SbCl_3 moieties are further linked to each other via bridging Cl atoms (Sb-Cl = 3.530(2) Å). The resulting intermolecular interactions gives rise to an extended one-dimensional polymeric structure. In this complex, the SbCl_3 groups behave as a Lewis acid and complex to $\text{TcCl}_4(\text{PMe}_2\text{Ph})_2$ through the chloride atoms and the phenyl ring of the phosphine. Similar polymeric Lewis base adducts have been observed between SbCl_3 and biphenyl. Clearly, the choice to use $[\text{SbCl}_6]^-$ as a counterion was a poor selection as the $[\text{SbCl}_6]^-$ counterion has become involved in the redox chemistry. This problem may be alleviated by replacement of $[\text{SbCl}_6]^-$ with the more robust $[\text{PF}_6]^-$ anion.

Oxidation of $\text{Tc}_2\text{Cl}_4(\text{PMe}_2\text{Ph})_4$ in the presence of Cl^- ion produced the neutral Tc(II)-Tc(III) species $\text{Tc}_2\text{Cl}_5(\text{PMe}_2\text{Ph})_3$ in good yield. The formation of 1,3,6- $\text{Tc}_2\text{Cl}_5(\text{PMe}_2\text{Ph})_3$ occurs via a sequential one electron oxidation followed by substitution of Cl^- for a phosphine ligand. Confirmation of this mechanism was provided by the observation that addition of ppnCl to a solution of $[\text{Tc}_2\text{Cl}_4(\text{PMe}_2\text{Ph})_4]^+$ yields $\text{Tc}_2\text{Cl}_5(\text{PMe}_2\text{Ph})_3$. A similar EC type mechanism has been postulated for the formation of $\text{Re}_2\text{Cl}_5(\text{PR}_3)_3$ and $\text{Re}_2\text{Cl}_6(\text{PR}_3)_2$ in electrochemically oxidized solutions of $\text{Re}_2\text{Cl}_4(\text{PR}_3)_4$ in the presence of Cl^- ion. The substitution chemistry is thought to be promoted by the reduction of the overall charge on the molecule that occurs upon replacement of a neutral phosphine donor for a chloride ligand. An X-ray crystallographic study shows that $\text{Tc}_2\text{Cl}_5(\text{PMe}_2\text{Ph})_3$ is structurally similar to $\text{Tc}_2\text{Cl}_4(\text{PMe}_2\text{Ph})_4$ and $[\text{Tc}_2\text{Cl}_4(\text{PMe}_2\text{Ph})_4]^+$ in that it consists of two eclipsed ML_4 fragments. However, one of the phosphine ligands has been replaced by a Cl^- ion. The isomer formed is the more sterically favored 1,3,6-isomer, where the phosphine ligands which reside on the same Tc atom are *trans* to one another. There is no disordering of the metal-metal unit within the ligand cage as was observed in the structure of 1,3,6- $\text{Re}_2\text{Cl}_5(\text{PEt}_3)_3$. The Tc-Tc bond length of 2.1088(5) Å is comparable to length observed for $\text{Tc}_2\text{Cl}_4(\text{PMe}_2\text{Ph})_4$ and is consistent with the presence of a Tc-Tc multiple bond. On the basis of the Tc_2^{5+} core, a $\sigma^2\pi^4\delta^2\delta^*1$ ground state electronic configuration is expected for $\text{Tc}_2\text{Cl}_5(\text{PMe}_2\text{Ph})_3$, giving rise to a formal bond order of 3.5. A cyclic voltammogram of $\text{Tc}_2\text{Cl}_5(\text{PMe}_2\text{Ph})_3$ reveals that two reversible redox processes are available. Indicative of a complex possessing a Tc_2^{5+} core, a reduction couple appears at -0.74 volts vs. Cp_2Fe and a one electron oxidation process is present at + 0.53 volts vs. Cp_2Fe . Both couples appear at more negative potentials than those observed for $[\text{Tc}_2\text{Cl}_4(\text{Me}_2\text{Ph})_4]^+$ due to the substitution of a π -donating Cl^- for a phosphine ligand. The results from the electrochemical study indicate that preparation of a series of complexes containing the

Tc_2^{4+} , Tc_2^{5+} and Tc_2^{6+} that are supported by an identical ligand set will be more feasible using $Tc_2Cl_5(PMe_2Ph)_3$, as both the oxidation and reduction processes are more chemically accessible.

Preparation of Diphosphine Complexes from $Tc_2Cl_4(PR_3)_4$

In addition to the rich redox chemistry displayed by $Tc_2Cl_4(PR_3)_4$ type complexes, these species also undergo phosphine substitution reactions with diphosphines such as dppe (bis-diphenyl phosphino ethane) and dppm (bis-diphenyl phosphino methane). $Tc_2Cl_4(PEt_3)_4$ reacts with excess dppe in refluxing toluene to produce a pale pink precipitate that analyzes as $Tc_2Cl_4(dppe)_2$. Similar results were obtained when dppm is substituted for dppe. However, the extreme insolubility of the product has precluded a definitive characterization.

The crystal structure of $Tc_2Cl_4(dppe)_2$ shows that it is isolated as the β -isomer in which the two dppe ligands bridge the two technetium centers rather than chelate. The formation of only the β -form of $Tc_2Cl_4(dppe)_2$ is not unexpected considering the thermal conditions used to obtain the product. The α forms of $M_2Cl_4(dppe)_2$, $M = Mo$ and Re , have been shown to thermally convert to the more stable β -isomer. β - $Tc_2Cl_4(dppe)_2$ is isostructural with both the Mo and Re derivatives. Unlike other $Tc_2Cl_4(PR_3)_4$ type complexes, the two $TcCl_2P_2$ fragments are staggered with respect to one another. When viewed down the $Tc-Tc$ bond the twist angle is approximately 30° . Replacement of the 4 monodentate phosphine ligands with dppe has removed some of the steric constraints that were present in parent complex and the molecule adopts a twisted conformation that better suits the bridging dppe ligands. The $P-C-C-P$ atoms of the bridging dppe ligands form 2 six-membered rings that include the 2 Tc atoms. These fused ring systems adopt chair conformations similar to that of cyclohexane. While the molecule has no crystallographic imposed symmetry, the overall symmetry of the molecule approaches D_2 . The $Tc-Tc$ separation of $2.116(1)$ Å is typical of triply bonded Tc_2^{4+} core and does not differ significantly from those found in the other $Tc_2Cl_4(PR_3)_4$ type complexes. Just as was observed for the Mo , W and Re derivatives, a second minor orientation of the metal-metal vector is found for β - $Tc_2Cl_4(dppe)_2$. The second orientation is present in 13% and lies perpendicular to the primary orientation.

A cyclic voltammogram of β - $Tc_2Cl_4(dppe)_2$ revealed the presence of only one reversible oxidation process at approximately 0.85 volts vs. Ag/Ag^+ . Accordingly, treatment of β - $Tc_2Cl_4(dppe)_2$ with one equivalent of $NOPF_6$ yielded a green product, presumably the complex salt $[\beta-Tc_2Cl_4(dppe)_2][PF_6]$.

Although $Tc_2Cl_4(PMe_2Ph)_4$ and $Tc_2Cl_4(PMePh)_4$ react with dppe to produce β - $Tc_2Cl_4(dppe)_2$, the α -isomer is obtained when $Tc_2Cl_4(PMePh_2)_4$ is used as the starting material. Reaction of $Tc_2Cl_4(PMePh_2)_4$ with a 10-fold excess of dppe in refluxing toluene resulted in the precipitation of α - $Tc_2Cl_4(dppe)_2$ in nearly 80% yield. A cyclic voltammogram of the product gave no indication for the presence of the β -isomer. The role that the monodentate phosphine plays in this reaction is not well understood. Apparently the increased steric bulk of $PMePh_2$ alters the

reaction mechanism allowing the formation of the less stable α -isomer which precipitates from solution. The α -form slowly isomerizes to β - $\text{Tc}_2\text{Cl}_4(\text{dppe})_2$ as evidenced by the isolation of β - $\text{Tc}_2\text{Cl}_4(\text{dppe})_2$ from pure samples of α - $\text{Tc}_2\text{Cl}_4(\text{dppe})_2$ during the recrystallization from CH_2Cl_2 . An X-ray crystallographic study of α - $\text{Tc}_2\text{Cl}_4(\text{dppe})_2$ shows that the Tc-Tc bond resides on an inversion center. The dppe ligands form a chelate with the metal centers requiring a cis-arrangement of the Cl groups. The two TcCl_2P_2 fragments are nearly eclipsed with the dppe ligands rotated 180° with respect to each other in an anti-eclipsed conformation. Although the molecule resides on a center of symmetry, the orientation of the ligands results in overall C_{2h} symmetry. The Tc-Tc bond distance of 2.141(2) Å is slightly longer than that observed for the β -isomer, a trend that also exists between the α - and β -isomers of $\text{Mo}_2\text{Cl}_4(\text{dppe})_2$, $\text{W}_2\text{Cl}_4(\text{dppe})_2$ and $\text{Re}_2\text{Cl}_4(\text{dppee})_2$. The origin of the lengthen results from the greater steric repulsion associated with the chelating geometry of the phosphines. With the phosphines bridging the metal centers, these steric interactions are diminished causing the M-M bond distance to contract slightly. The lowering of steric barriers are also evident from the staggered conformation of β - $\text{Tc}_2\text{Cl}_4(\text{dppe})_2$ versus the eclipsed conformation of the α -isomer. Unlike the structure of the β -isomer, only one orientation of the Tc-Tc bond is present in α - $\text{Tc}_2\text{Cl}_4(\text{dppe})_2$. The two isomeric forms of $\text{Tc}_2\text{Cl}_4(\text{dppe})_2$ are related by internal orientation of the Tc-Tc bond (or internal flip) inside the nearly cubic cage of phosphorus and chloride atoms. A reorientation of the Tc-Tc bond in α - $\text{Tc}_2\text{Cl}_4(\text{dppe})_2$ by 90° would produce the β -isomeric form. It was shown that such a process occurs unimolecularly for α - $\text{Mo}_2\text{Cl}_4(\text{dppe})_2$ and α - $\text{Mo}_2\text{Br}_4(\text{dppe})_2$.

$[\text{Tc}_2(\text{CH}_3\text{CN})_{10}][\text{BF}_4]_4$

(a) Synthesis and Characterization. Previously we had shown that $[\text{Tc}_2(\text{CH}_3\text{CN})_{10}][\text{BF}_4]_4$ may be prepared in high yield from $\text{Tc}_2\text{Cl}_4(\text{PET}_3)_4$. We have further extended the synthesis to include the use of other $\text{Tc}_2\text{Cl}_4(\text{PR}_3)_4$ species as precursors. Both $\text{Tc}_2\text{Cl}_4(\text{Me}_2\text{Ph})_4$ and $\text{Tc}_2\text{Cl}_4(\text{PMePh}_2)_4$ may be used to prepare $[\text{Tc}_2(\text{CH}_3\text{CN})_{10}][\text{BF}_4]_4$ in yields comparable to those achieved with $\text{Tc}_2\text{Cl}_4(\text{PET}_3)_4$. The primary advantage of using aryl-phosphine derivatives is the ease of preparation of the starting materials $\text{TcCl}_4(\text{PMe}_2\text{Ph})_2$ and $\text{TcCl}_4(\text{PMePh}_2)_2$, which unlike the PET_3 derivative, may be prepared directly from $[\text{NH}_4][\text{TcO}_4]$ in one step. Currently, $\text{Tc}_2\text{Cl}_4(\text{PMePh}_2)_4$ is used exclusively to prepare $[\text{Tc}_2(\text{CH}_3\text{CN})_{10}][\text{BF}_4]_4$. Several attempts have been made to prepare $[\text{Tc}_2(\text{CH}_3\text{CN})_{10}][\text{BF}_4]_4$ directly from the $[\text{TcO}_4]^-$ anion. Reduction of $[\text{NH}_4][\text{TcO}_4]$ in acetonitrile with zinc metal in the presence of HBF_4 produces an insoluble black precipitate believed to be TcO_2 . Apparently, in the absence of a suitable ligand environment, the intermediate oxidation states are unstable and formation of TcO_2 become a thermodynamic sink. Interestingly, zinc reduction of $\text{TcCl}_4(\text{PPh}_3)_2$ followed by treatment with HBF_4 in acetonitrile does not produce $[\text{Tc}_2(\text{CH}_3\text{CN})_{10}][\text{BF}_4]_4$. Presumably, the bulk of the PPh_3 ligands prevents

formation of a dinuclear intermediate thereby thwarting the formation of $[\text{Tc}_2(\text{CH}_3\text{CN})_{10}][\text{BF}_4]_4$. This suggests that pre-formation of a metal-metal bond is required in order to prepare $[\text{Tc}_2(\text{CH}_3\text{CN})_{10}][\text{BF}_4]_4$.

After several unsuccessful attempts at obtaining a satisfactory X-ray structure refinement of $[\text{Tc}_2(\text{CH}_3\text{CN})_{10}][\text{BF}_4]_4$, we chose to pursue a structural determination of the $[\text{Tc}_2(\text{CH}_3\text{CN})_{10}]^{4+}$ molecular cation using other anions. Addition of 8 equivalents of $\text{Tl}(\text{O}_3\text{SCF}_3)$ to an acetonitrile solution of $[\text{Tc}_2(\text{CH}_3\text{CN})_{10}][\text{BF}_4]_4$ followed by slow diffusion of diethyl ether produces large crystals of the bis-triflate salt $[\text{Tc}_2(\text{CH}_3\text{CN})_8(\text{O}_3\text{SCF}_3)_2][\text{BF}_4]_2$. The molecular geometry consists of two $\text{Tc}(\text{CH}_3\text{CN})_4$ fragments bound together by a short Tc-Tc triple bond. The pseudo-planar fragments are staggered with respect to one another resulting in a torsion angle between the fragments of $43.5 [1]^\circ$. The staggered geometry observed for $[\text{Tc}_2(\text{CH}_3\text{CN})_8(\text{O}_3\text{SCF}_3)_2][\text{BF}_4]_2$ is a consequence of the electron rich triple bond which exists between the metal centers. The d^5 - d^5 electronic configuration results in filling of both the δ and δ^* molecular orbitals leading to no net δ -bond between the metal centers. Consequently, there is no electronic barrier to rotation about the metal-metal bond and the molecule adopts the sterically favored conformation. Similar torsion angles are observed for $[\text{Re}_2(\text{CH}_3\text{CN})_{10}][\text{Mo}_6\text{O}_{18}]_2$ and $[\text{Rh}_2(\text{CH}_3\text{CN})_{10}][\text{BF}_4]_4$, which also do not contain a δ -component in their bonding. However, $[\text{Mo}_2(\text{CH}_3\text{CN})_{10}][\text{BF}_4]_4$, which contains a metal-metal quadruple bond, adopts an eclipsed geometry consistent with the presence of a δ bond. Although $[\text{Tc}_2(\text{CH}_3\text{CN})_8(\text{O}_3\text{SCF}_3)_2][\text{BF}_4]_2$ adopts a staggered conformation in the solid state, we expect that the steric barrier to rotation is easily overcome in solution, allowing the molecule to rotate freely about the metal-metal bond. Excluding the axial triflate molecules, the staggered conformation of the ML_4 fragments gives the molecular cation pseudo D_{4d} symmetry. The Tc-Tc bond lies perpendicular to a two-fold axis giving the cation crystallographically imposed C_2 symmetry. The metal-metal bond distance of $2.122 (1)\text{\AA}$ is characteristic of a multiple bond between the Tc atoms. Comparison with other technetium triply bonded complexes shows that the Tc-Tc bond distance in $[\text{Tc}_2(\text{CH}_3\text{CN})_8(\text{O}_3\text{SCF}_3)_2][\text{BF}_4]_2$ is slightly shorter than that observed for $\text{Tc}_2\text{Cl}_4(\text{PR}_3)_4$ ($2.127(1) - 2.1384(5)\text{\AA}$), but longer than that observed in the polymeric chain complex $[\text{Tc}_2\text{Cl}_6]_n^{2n-}$ ($2.044 (1)\text{\AA}$). The axial positions of the dinuclear unit are occupied by weakly interacting triflate anions at a distance of $2.414 (6)\text{\AA}$. The long interaction is indicative of the weak donor ability of the triflate anion and the strong trans-effect imparted by the metal-metal multiple bond. We anticipate that in acetonitrile, these anions are readily displaced by solvent molecules. All Tc-N distances are within the range normally anticipated for such bonds. The BF_4^- anion resides on a general position within the unit cell and does not interact with the dinuclear unit.

The infrared spectrum of $[\text{Tc}_2(\text{CH}_3\text{CN})_{10}][\text{BF}_4]_4$ exhibits characteristic $\nu(\text{C}\equiv\text{N})$ stretching vibrations at 2330 and 2302 cm^{-1} corresponding to coordinated acetonitrile ligands. The presence of BF_4^- is readily discernible by the appearance of a strong B-F stretch near 1064 cm^{-1} . $^1\text{H NMR}$

spectroscopy of $[\text{Tc}_2(\text{CH}_3\text{CN})_{10}][\text{BF}_4]_4$ in CD_3NO_2 , a non-coordinating solvent, 2 separate resonances are observed at δ 3.00 ppm and δ 2.00 in a ratio of 4:1. These resonances are assigned to the equatorial and dissociated axial nitrile ligands, respectively. The ^1H NMR in CD_3CN initially shows resonances corresponding to equatorially coordinated CH_3CN at 2.95 ppm and free nitrile at 1.95 ppm. However, as substitution of the coordinated CH_3CN for CD_3CN takes place the intensity of the resonance decreases until only a single resonance attributable to free nitrile is observed. The sharp and unshifted nature of these resonances suggest that the molecule is diamagnetic, consistent with the presence of an electron-rich triple bond between the metal centers. The electronic spectrum of $[\text{Tc}_2(\text{CH}_3\text{CN})_{10}][\text{BF}_4]_4$ in acetonitrile exhibits a broad absorption at 616 nm ($120 \text{ M}^{-1} \text{ cm}^{-1}$) giving the complex its blue color. The low molar absorptivity of the transition is in accordance with a metal-metal based $\delta^* - \pi^*$ transition. Higher energy absorptions are present at 312 nm ($360 \text{ M}^{-1} \text{ cm}^{-1}$) and 260 nm ($1500 \text{ M}^{-1} \text{ cm}^{-1}$).

(b) Photochemistry of $[\text{Tc}_2(\text{CH}_3\text{CN})_{10}][\text{BF}_4]_4$ Acetonitrile solutions of $[\text{Tc}_2(\text{CH}_3\text{CN})_{10}][\text{BF}_4]_4$, when exposed to room light over a period of several days, gradually lose their intense blue color and become colorless. Work-up of the colorless solution by addition of diethyl ether gives the salmon colored mononuclear species $[\text{Tc}(\text{CH}_3\text{CN})_6][\text{BF}_4]_2$. Using a 300 watt tungsten lamp, the conversion of $[\text{Tc}_2(\text{CH}_3\text{CN})_{10}][\text{BF}_4]_4$ to $[\text{Tc}(\text{CH}_3\text{CN})_6][\text{BF}_4]_2$ occurs over a period of 12 to 24 hours. For preparative scale reactions, a 1000 w Hg vapor lamp was used. After only 90 minutes of irradiation with the Hg lamp, the mononuclear species was isolated in 95% yield by careful addition of diethyl ether.

Red-orange single crystals of $[\text{Tc}(\text{CH}_3\text{CN})_6][\text{BF}_4]_2$ were obtained by slow diffusion of diethyl ether into a solution of $[\text{Tc}(\text{CH}_3\text{CN})_6][\text{BF}_4]_2$ in acetonitrile. An X-ray diffraction study of $[\text{Tc}(\text{CH}_3\text{CN})_6][\text{BF}_4]_2$ revealed that the Tc center is ligated by six acetonitrile ligands in an octahedral arrangement. A slight distortion of the N-Tc-N angles from 90° results in the lowering of the idealized molecular symmetry from O_h symmetry to the crystallographically imposed C_i symmetry. The 3 crystallographically independent Tc-N bond distances are only slightly longer than those reported for $[\text{Ru}(\text{CH}_3\text{CN})_6][\text{PF}_6]_2$, but similar to those found for the equatorial acetonitrile ligands of $[\text{Tc}_2(\text{CH}_3\text{CN})_8(\text{O}_3\text{SCF}_3)_2][\text{BF}_4]_2$. The nitrogen and carbon bond distances and angles of the coordinated acetonitrile ligands fall within the expected ranges. A solid state IR spectrum of $[\text{Tc}(\text{CH}_3\text{CN})_6][\text{BF}_4]_2$ reveals weak absorptions at 2319 and 2280 cm^{-1} attributed to the $\text{C}\equiv\text{N}$ stretching vibrations. The presence of the $[\text{BF}_4]^-$ counterion was confirmed by the observation of a strong band at 1065 cm^{-1} . The electronic spectrum of $[\text{Tc}(\text{CH}_3\text{CN})_6][\text{BF}_4]_2$ in acetonitrile exhibits no observable absorption bands in the visible region, accounting for the nearly colorless appearance of $[\text{Tc}(\text{CH}_3\text{CN})_6][\text{BF}_4]_2$ in solution. The lowest energy transition appears at 335 nm and tails slightly into the visible region, giving concentrated solutions of $[\text{Tc}(\text{CH}_3\text{CN})_6][\text{BF}_4]_2$ a faint yellow color. In spite of the paramagnetism of the Tc(II) cation, a ^1H

NMR spectrum in CD₃CN can be obtained. A broad and highly shifted resonance corresponding to the coordinated acetonitrile ligands appears at 70.3 ppm. Ultimately, the coordinated nitrile ligands exchange with the deuterated solvent and only a resonance attributable to unligated CH₃CN is observed.

Remarkably, the Tc(II) cation is high spin in solution as evidenced by room temperature magnetic susceptibility measurements. The solution paramagnetism of [Tc(CH₃CN)₆][BF₄]₂, investigated by the Evans method, demonstrates the existence of a $S = 5/2$ ground state ($\mu_{\text{eff}} = 6.1$ BM). The presence of a ⁶A_{1g} ground state in solution accounts for the absence of any observable absorptions in the visible spectrum of [Tc(CH₃CN)₆][BF₄]₂. For a high-spin d⁵ configuration, all d-d transitions are strongly forbidden and are presumably masked by the strong absorption at 335 nm. Despite the evidence for a ⁶A_{1g} ground state in solution, the presence of a high-spin d⁵ electronic configuration is expected to lengthen the Tc-N bond distances by 0.15–0.20 Å relative to a low-spin configuration. Yet, a comparison of metal–nitrile bond lengths of [Tc(CH₃CN)₆][BF₄]₂ with those observed for [Ru(CH₃CN)₆][PF₆]₂ illustrates that the metal–ligand bond distances are nearly identical to those found in the diamagnetic Ru(II) system. A solid state magnetic susceptibility measurement of the precipitated solid shows a gradual spin-state transition from one unpaired electron near 5 K to 5 unpaired electrons at room temperature. Magnetic measurements on the single crystalline phase are forthcoming.

The magnetic behavior of [Tc(CH₃CN)₆][BF₄]₂ is unprecedented for a second-row transition metal ion as it represents the first example of a high-spin coordination complex for a second-row transition metal element. The serendipitous combination of a half-filled d-manifold, a low metal oxidation state and ligation by a relatively weak field ligand contributes to the observed magnetic behavior of [Tc(CH₃CN)₆][BF₄]₂. Apparently, the cubic ligand field strength is nearly equal to the exchange energy with the difference in energy between the two spin-states being on the order of kT.

A cyclic voltammogram of [Tc(CH₃CN)₆][BF₄]₂ in acetonitrile exhibits a reversible reduction at – 0.81 V and a quasi-reversible oxidation at + 0.72 V vs Cp₂Fe. The presence of the oxidation couple is surprising since such a process was not observed for [Tc₂(CH₃CN)₁₀][BF₄]₄ and does not occur for [Ru(CH₃CN)₆]²⁺. The ability to oxidize [Tc(CH₃CN)₆][BF₄]₂ in solution may be directly related to the presence of the high-spin ground state, i.e. removal of an electron from an e_g orbital is expected to be more favorable than removal from a lower energy t_{2g} orbital.

The photolysis of [Tc₂(CH₃CN)₁₀][BF₄]₄ represents a rare example of a photochemical cleavage of a metal–metal multiple bond. Preliminary results indicate that under the same photolytic conditions, the Re–Re triple bond in [Re₂(CH₃CN)₁₀][BF₄]₄ and the Mo–Mo quadruple bond in [Mo₂(CH₃CN)₁₀][BF₄]₄ do not undergo metal–metal bond homolysis. Solutions of [Tc₂(CH₃CN)₁₀][BF₄]₄ are stable with respect to metal–metal bond cleavage in refluxing

acetonitrile. In fact, $[\text{Tc}_2(\text{CH}_3\text{CN})_{10}][\text{BF}_4]_4$ is prepared under refluxing conditions from $\text{Tc}_2\text{Cl}_4(\text{PR}_3)_4$ ($\text{PR}_3 = \text{PEt}_3, \text{PMe}_2\text{Ph}$ or PMePh_2) or $[\text{Bu}_4\text{N}]_2[\text{TcCl}_6]$. This demonstrates that metal-metal bond homolysis of $[\text{Tc}_2(\text{CH}_3\text{CN})_{10}][\text{BF}_4]_4$ does not occur thermally. Irradiation into the broad absorption band at 616 nm appears to be responsible for the observed photochemistry. Excitation at 514.5 nm using an Ar laser results in rapid bleaching of the blue solution signifying the formation of $[\text{Tc}(\text{CH}_3\text{CN})_6][\text{BF}_4]_2$. Irradiation at 633 nm using a He/Ne laser also leads to metal-metal bond cleavage but at a much slower rate. It is believed that the 616 nm band corresponds to a δ^* to π^* transition based on comparisons with other $[\text{Re}_2]^{4+}$ and $[\text{Tc}_2]^{4+}$ complexes. Monitoring the reaction by electronic spectroscopy reveals that metal-metal bond cleavage of $[\text{Tc}_2(\text{CH}_3\text{CN})_{10}][\text{BF}_4]_4$ is not a simple process, but instead involves the formation of at least one intermediate prior to formation of $[\text{Tc}(\text{CH}_3\text{CN})_6]^{2+}$. After 5 min of photolysis with a Hg lamp, several new absorption bands are evident. A broad transition appears at 1100 nm together with two lower energy bands at 490 and 405 nm. Furthermore, the band at 616 nm undergoes a slight blue shift and increase in intensity. As the reaction progresses, these bands disappear leaving the nearly featureless spectrum of $[\text{Tc}(\text{CH}_3\text{CN})_6][\text{BF}_4]_2$. Irradiation of $[\text{Tc}_2(\text{CH}_3\text{CN})_{10}][\text{BF}_4]_4$ with a 300 watt incandescent tungsten lamp results in the formation of the similar absorption bands, however, 490 nm band does not decrease in intensity at the same rate as the 1100 nm and 405 nm bands indicating that the 490 nm chromophore is a separate chemical entity. The cleavage process is irreversible as there is no evidence for an equilibrium between $[\text{Tc}_2(\text{CH}_3\text{CN})_{10}][\text{BF}_4]_4$ and $[\text{Tc}(\text{CH}_3\text{CN})_6][\text{BF}_4]_2$. The low energy band at 1100 nm is reminiscent of the low energy δ - δ^* transitions found for many $\text{Tc}_2(\text{II,III})$ $\text{Re}_2(\text{II,III})$ complexes and may implicate the intermediacy of a mixed valent dinuclear complex. Such an intermediate is plausible assuming that irradiation of $[\text{Tc}_2(\text{CH}_3\text{CN})_{10}][\text{BF}_4]_4$ produced a long-lived excited state species, $[\text{Tc}_2]^{4+*}$, which then participates in an electron transfer process to form a mixed valent complex. Similar photoinduced redox processes are well-established for quadruply bonded dimolybdenum and dirhenium compounds. For example, the ${}^1\delta\delta^*$ excited state of $[\text{Re}_2\text{Cl}_8]^{2-}$ was determined to be a powerful one-electron oxidant and a moderately strong one-electron reductant. Photoexcitation of $[\text{Re}_2\text{Cl}_8]^{2-}$ in the presence of various electron donors and acceptors resulted in generation of the mixed valence species $[\text{Re}_2\text{Cl}_8]^{3-}$ and $[\text{Re}_2\text{Cl}_8]^{1-}$. Back electron-transfer was circumvented by further reaction of $[\text{Re}_2\text{Cl}_8]^{1-}$ with chloride ion. By analogy, back electron-transfer of the photogenerated Tc species may be averted by chemical decomposition of either the donor or acceptor allowing the dinuclear metal species to ultimately undergo metal-metal bond cleavage to produce $[\text{Tc}(\text{CH}_3\text{CN})_6][\text{BF}_4]_2$. However, detection of a long-lived excited state in either solution or the solid has proven elusive. Suffice it to say, the chemical identities of the photogenerated intermediates are presently unknown and the photochemical pathway may only be

speculated upon. Consequently, further investigations into complex photochemistry of $[\text{Tc}_2(\text{CH}_3\text{CN})_{10}][\text{BF}_4]_4$ are warranted.

(c) **Redox Chemistry of $[\text{Tc}_2(\text{CH}_3\text{CN})_{10}][\text{BF}_4]_4$.** As was noted previously, $[\text{Tc}_2(\text{CH}_3\text{CN})_{10}][\text{BF}_4]_4$ is readily reduced by either Zn or Cp_2Co in acetonitrile to give the dark red-brown product $[\text{Tc}_2(\mu, \eta^2\text{-CH}_3\text{CN})(\text{CH}_3\text{CN})_{10}][\text{BF}_4]_3$ in roughly 70% yield. An IR spectrum of $[\text{Tc}_2(\mu, \eta^2\text{-CH}_3\text{CN})(\text{CH}_3\text{CN})_{10}][\text{BF}_4]_3$ shows absorptions due to two types of $\text{C}\equiv\text{N}$ stretches; terminal modes at 2277 cm^{-1} and 2256 cm^{-1} , and a η^2 -stretch at 1822 cm^{-1} . A strong, broad charge-transfer band is observed at 1228 nm and tails into the visible region accounting for the dark red-brown color of this species. A preliminary structure determination reveals two non-bonded Tc centers that are bridged by an acetonitrile ligand that is σ -bonded to one Tc center and π -bonded in a η^2 fashion to the other. Both metal atoms exhibit an octahedral coordination environment with the remaining coordination sites occupied by nitrile ligands. The Tc-Tc separation of $>3\text{ \AA}$ indicates there is no metal-metal bonding present. The two metal centers and η^2 -nitrile ligand are nearly co-planar. While the $\mu_2, \eta^2\text{-C}\equiv\text{N}$ bond distance of approximately 1.2 \AA is slightly elongated, it is not far outside the range expected for a $\text{C}\equiv\text{N}$ triple bond. This unusual complex represents a rare example of a structurally determined bridging $\eta^2\text{-CH}_3\text{CN}$ ligand. Evidently, reduction of $[\text{Tc}_2(\text{MeCN})_{10}]^{4+}$ yields the corresponding $[\text{Tc}_2(\text{MeCN})_{10}]^{3+}$ species which is not stable and rearranges to the observed $[\text{Tc}_2(\mu, \eta^2\text{-MeCN})(\text{MeCN})_{10}]^{3+}$. Time dependent Uv-vis studies of the reaction, however, do not indicate the presence of an intermediate species. This observation has one of two implications. The intermediate is too short lived and does not build up enough to be detect by visible spectroscopy or the spectrum of the intermediate species is masked by the intense charge transfer band of $[\text{Tc}_2(\mu, \eta^2\text{-MeCN})(\text{MeCN})_{10}]^{3+}$.

Electrochemical studies of $[\text{Tc}_2(\mu, \eta^2\text{-MeCN})(\text{MeCN})_{10}][\text{BF}_4]_3$ reveal the presence of a reversible reduction at $E_{1/2} = -1.12\text{ V}$, a reversible oxidation at $E_{1/2} = -0.25\text{ V}$ vs. Cp_2Fe followed by an electrochemically irreversible oxidation process at $E_{p,a} = +0.79\text{ V}$. The amount of charge carried by the second wave is approximately twice that of the reversible couples. The reversibility of the first oxidation process and reduction couple suggest that addition or removal of one electron does not result in any significant structural changes, at least on the time scale of the experiment. The reversibility of the first oxidation process is significant in that it implicates the exists of yet another isomer for Tc(II) nitrile species. However, experimentally, chemical oxidation of $[\text{Tc}_2(\mu, \eta^2\text{-MeCN})(\text{MeCN})_{10}][\text{BF}_4]_3$ with $[\text{Cp}_2\text{Fe}][\text{PF}_6]$ results in cleavage of the $(\mu, \eta^2\text{-MeCN})$ linkage and only the mononuclear species $\text{Tc}(\text{CH}_3\text{CN})_6^{2+}$ is produced. The stability of the $(\mu, \eta^2\text{-MeCN})$ linkage upon chemical reduction is unknown.

Formamidinate Complexes

Formamidinate complexes of technetium may be readily prepared by the reaction of $\text{Tc}_2\text{Cl}_4(\text{PR}_3)_4$ with molten formamidine. Under the extreme thermal conditions, the relatively labile

phosphine is driven off, while the chloride ligand becomes protonated and is removed as HCl (g). Concomitantly, the metal center is oxidized during the reaction, presumably at the expense of some of the formamidine. Depending on the reaction conditions employed, two primary products have been isolated. Shorter reaction times yield tris-bridged species $\text{Tc}_2(\text{DPhF})_3\text{Cl}_2$ while longer times tend to favor formation of the tetra bridged complex $\text{Tc}_2(\text{DPhF})_4\text{Cl}$. A single-crystal X-ray structure determination of $\text{Tc}_2(\text{DTolF})_3\text{Cl}_2$ shows that the molecule adopts an eclipsed conformation with the two chloride ligands in a *syn*-orientation. Although the molecule does not have any crystallographically imposed symmetry, the *syn* arrangement of the chloride ligands gives it pseudo C_{2v} symmetry. The Tc-Tc bond distance of 2.093 Å is consistent with those observed for other Tc(II)-Tc(III) dinuclear species. The solid state structure of $\text{Tc}_2(\text{DPhF})_4\text{Cl}$ reveals that the four formamidinate ligands bridge the metal centers in a typical lantern type structure common among all other tetra-formamidinate complexes. The chloride atom occupies one of the axial positions of the dinuclear core. The Tc-Tc bond distance of 2.119(2) Å does not significantly differ from that observed for $\text{Tc}_2(\text{DTolF})_3\text{Cl}_2$.

As expected for a complex containing a Tc_2^{5+} core, $\text{Tc}_2(\text{DTolF})_3\text{Cl}_2$ is paramagnetic. An ESR spectrum of $\text{Tc}_2(\text{DTolF})_3\text{Cl}_2$ at 15K exhibits a broad signal at $g = 2.12$. Although not well resolved, some Tc and N hyperfine coupling is evident. Electrochemical studies of $\text{Tc}_2(\text{DTolF})_3\text{Cl}_2$ in CH_2Cl_2 reveal the presence of two reversible redox processes corresponding to an oxidation at -0.2 volts vs. ferrocene and a reduction at -1.5 volts vs. ferrocene.

The synthetic strategy that was used to prepare $\text{Tc}_2(\text{DTolF})_3\text{Cl}_2$ and $\text{Tc}_2(\text{DPhF})_4\text{Cl}$ was extended to dirhenium chemistry. The reaction of $\text{Re}_2\text{Cl}_4(\text{PEt}_3)_4$ with molten HDPhF produces the $\text{Re}_2^{\text{III,III}}$ species $\text{Re}_2(\text{DTolF})_4\text{Cl}_2$ in good yield. In refluxing toluene, only the partially substituted complex $\text{Re}_2(\text{DTolF})_3\text{Cl}_3$ is formed. In both examples, the Re_2^{4+} core has been fully oxidized to the quadruply bonded Re_2^{6+} core. This illustrates a primary difference between the chemistry of Tc and Re. Typical of many third row transition metals, the analogous rhenium complexes tend to be more stable in higher oxidation states than the corresponding Tc species. The molecular structure of $\text{Re}_2(\text{DTolF})_3\text{Cl}_3$ is quite similar to that of $\text{Tc}_2(\text{DTolF})_3\text{Cl}_2$. The three formamidinate ligands bridge the two rhenium centers. Two of the chlorine atoms are coordinated in equatorial positions and lie in a *syn*-disposition. The third chloride ion resides in an axial position. The noticeably longer Re-Cl distance for the axial (Re-Cl = 2.445(2) Å) versus equatorial (Re-Cl = 2.370(2) Å) Cl atoms is a reflection of the strong *trans* influence imparted by the Re-Re bond. The Re-Re separation is 2.2327(9) Å, consistent with the presence of a Re-Re quadruple bond.

The novel structural nature of $\text{Tc}_2(\text{DTolF})_3\text{Cl}_2$ and $\text{Re}_2(\text{DTolF})_3\text{Cl}_3$ presents an opportunity for additional reactivity studies. Typically such lantern type complexes with four bridging ligands react via initial attack at the more accessible axial positions. However, the replacement of one of the bridging ligand with two chloride groups creates the opportunity for chemistry to occur directly at

the metal-metal bond. Removal of the equatorial chloride ligands is expected open up one face of dinuclear core and provide direct access to the metal-metal bond. The remaining three formamidinate bridges would then help support the dimetal unit and prevent fragmentation into mononuclear species. Such a situation may lead to highly reactive species and unprecedented chemistry for metal-metal multiply bonded complexes. We are also exploring the applicability of this synthetic methodology to prepare $M_2Cl_2(DPhF)_3$ type complexes for Mo and W.

Conclusion

As this project reaches its completion, most of our original goals have been achieved. The results of which will be published in a series of forthcoming papers that are currently being drafted. The number of well characterized Tc complexes containing a metal-metal multiple bond have been dramatically expanded to include complexes supported by phosphines, nitriles, and formamidinate ligands. We have developed a number new synthetic routes to several of these complexes. The various synthetic pathways that have been developed for the preparation of the new Tc complexes presented in this study are illustrated in figure 1. This study has established the use of $Tc_2Cl_4(PR_3)_4$ type complexes as precursors for the synthesis of a number of new ditechneium species containing a metal-metal multiple bond. As anticipated, $Tc_2Cl_4(PMe_2Ph)_4$ can be readily oxidized to form the Tc_2^{5+} species. Unfortunately the relatively high positive potential of the second oxidation process has precluded isolation of the quadruply bonded technetium species $[Tc_2Cl_4(PMe_2Ph)_4]^{2+}$. Electrochemical studies of $Tc_2Cl_5(PMe_2Ph)_3$ obtained by oxidation of $Tc_2Cl_4(PMe_2Ph)_4$ in the presence of Cl^- , indicate that substitution of one phosphine ligand for a chloride makes formation of the quadruply bonded species more accessible. In addition to its redox chemistry, $Tc_2Cl_4(PR_3)_4$ ($PR_3 = PEt_3, PMe_2Ph$ and $PMePh_2$) undergoes a variety of ligand substitution reactions. Reaction of bis-diphosphinoethane (dppe) with $Tc_2Cl_4(PR_3)_4$ yields the either the chelating or bridging forms of the bis-diphosphine complex $Tc_2Cl_4(dppe)_2$ depending on the type of phosphine ligand present in the precursor. Reactions of $Tc_2Cl_4(PR_3)_4$ with molten formamidine produce the tris- and tetra formamidinate complexes $Tc_2(DTolF)_3Cl_2$ and $Tc_2(DPhF)_4Cl$. Perhaps the most significant result has been the high yield synthesis of $[Tc_2(CH_3CN)_{10}][BF_4]_4$. This dinuclear core ligated solely by solvent molecules may be prepared from either $Tc_2Cl_4(PR_3)_4$ or $[TcCl_6]^{2-}$. While the substitution chemistry of $[Tc_2(CH_3CN)_{10}][BF_4]_4$ and $[Tc(CH_3CN)_6][BF_4]_2$ has yet to be fully investigated, we anticipate that these complexes will prove to be a valuable precursors in the study of the fundamental coordination chemistry of Tc. Of particular interest is the use of such nitrile species to prepare complexes of Tc supported by biologically relevant molecules. The lability of the nitrile ligands should make $[Tc_2(CH_3CN)_{10}][BF_4]_4$ and $[Tc(CH_3CN)_6][BF_4]_2$ ideal precursors for the incorporation of Tc into macrocyclic systems. However before nitrile complexes become important

in the pursuit of new radioimaging agents, a method must be developed for the preparation of nitrile species easily and directly from the $[\text{TcO}_4]^-$ anion.

The novel photochemistry of $[\text{Tc}_2(\text{CH}_3\text{CN})_{10}][\text{BF}_4]_4$ has provided the first example of a high spin second-row transition metal complex. The magnetic properties of $[\text{Tc}(\text{CH}_3\text{CN})_6][\text{BF}_4]_2$ are unprecedented for a second-row transition metal complex and represent the first example of spin-crossover system for an element other than a first row transition metal. The phenomenon of spin-crossover is still an area of intense research and provides impetus for preparing other second and third row metal complexes that may exhibit similar magnetic behavior. One potential candidate is the analogous d^5 molybdenum complex $[\text{Mo}(\text{CH}_3\text{CN})_6][\text{BF}_4]$. Particularly since the reduced charge on the metal should further lower the gap between the t_{2g} and e_g orbitals making the high-spin state even more energetically accessible. Efforts are underway to prepare d^5 and d^6 homoleptic nitrile complexes of Mo and investigate their magnetic behavior.

As this project draws to a conclusion, several avenues of further research remain to be investigated. This project has not only given us a better understanding of the coordination behavior of ditechneium but has also opened up new areas of chemistry that remain to be explored. The novel redox and photochemistry exhibited by $[\text{Tc}_2(\text{CH}_3\text{CN})_{10}][\text{BF}_4]_4$ provides the impetus for further investigation of the analogous Mo_2^{4+} and Re_2^{4+} nitrile systems. The approach used to prepare $\text{Tc}_2\text{Cl}_4(\text{PR}_3)_4$ may be applied to Ru and Os in order to prepare similarly supported systems. The preparation of tris-formamidinate complexes for ditechneium has led to the preparation of the analogous Re species and such an approach may be useful for the development of tris-formamidinate complexes of Mo_2 . In fact, such systems are attractive areas for future research because of their demonstrated rich redox chemistry and the potential for further reactivity through removal of the equatorial chloride ligands.

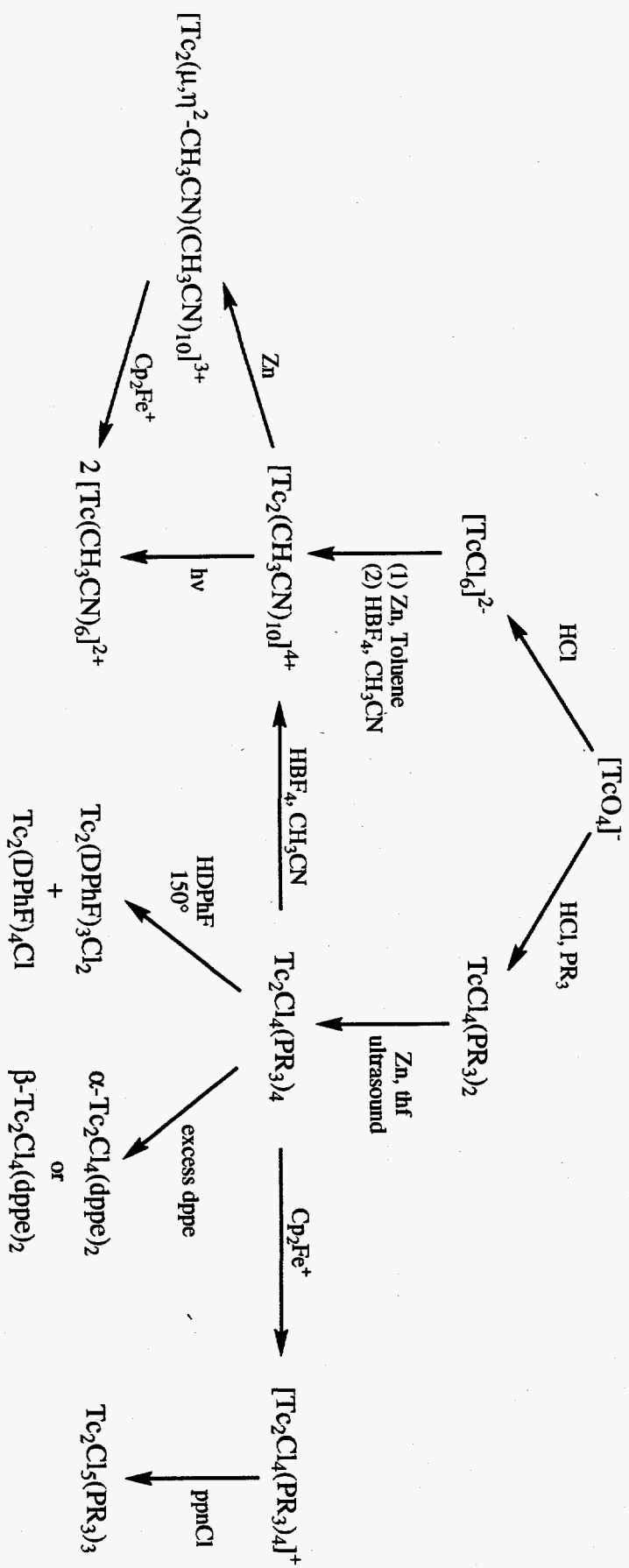


Figure 1. Synthetic Routes to Metal-Metal Bonded Complexes of Technetium