THE SYNTHESIS AND REACTIVITY OF LOW VALENT TECHNETIUM NITROSYL COMPLEXES

by
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ABSTRACT

Chapter 1. Two technetium(I) nitrosyl solvate complexes of the type $[Tc(NO)Cl_2(PPh_3)_2L]$ were synthesized from n-$Bu_4N[Tc(NO)Cl_4]$ and excess triphenylphosphine in the solvents acetonitrile and methanol (L); no reaction was observed in neat dimethylsulfoxide. The complexes were characterized by elemental analysis, mass spectrometry, infrared, ^1H and ^{99}Tc-NMR spectroscopy. Analysis of $[Tc(NO)Cl_2(PPh_3)_2(NCCH_3)]$ by ^1H-NMR spectroscopy shows that the acetonitrile molecule is labile, as it dissociates in solution and exchanges with added CD_3CN; a comparison is made with the rhenium analog, $[Re(NO)Cl_2(PPh_3)_2(NCCH_3)]$. The geometry of $[Tc(NO)Cl_2(PPh_3)_2(HOCH_3)]$ is shown to differ from that of the acetonitrile derivative in solution. While conversion from $[Tc(NO)Cl_2(PPh_3)_2(HOCH_3)]$ to $[Tc(NO)Cl_2(PPh_3)_2(NCCH_3)]$ is achieved through addition of excess acetonitrile, the reverse reaction is not observed. The reaction of n-$Bu_4N[Tc(NO)Cl_4]$ with excess triphenylphosphine in pyridine (py) gives $[Tc(NO)Cl_2(py)_3]$ as the major product, not $[Tc(NO)Cl_2(PPh_3)_2(py)]$. The straightforward preparation of $[Tc(NO)Cl_2(py)_3]$ from n-$Bu_4N[Tc(NO)Cl_4]$ in refluxing pyridine is described and found to be analogous to that of the known bromine analog.

Chapter 2. Ligand exchange reactions of $[Tc(NO)Cl_2(PPh_3)_2(NCCH_3)]$ with aromatic amines are described. The reaction of $[Tc(NO)Cl_2(PPh_3)_2(NCCH_3)]$ with pyridine results in stepwise substitution of the neutral ligands to yield the technetium(I) complexes $[Tc(NO)Cl_2(PPh_3)_2(py)]$, $[Tc(NO)Cl_2(PPh_3)(py)_2]$, or $[Tc(NO)Cl_2(py)_3]$, depending on the reaction conditions employed. Analogous complexes can be prepared using the bulkier pyridine ligand 3,5-lutidine and the multidentate aromatic amines 2,2'-bipyridine, 1,10-phenanthroline, and 2,2':6',2"-terpyridine. All of the complexes were characterized by elemental analysis, infrared and mass spectral data, as well as by ^1H and ^{99}Tc-NMR spectroscopy. A single crystal X-ray structure determination of $[Tc(NO)Cl_2(py)_3]\cdot 2CH_3CN$ shows an essentially octahedral coordination geometry with the three pyridine ligands positioned in a meridional configuration, *cis* to the linear nitrosyl group. A two-fold site disorder is evident along the *trans*Cl-Tc-NO axis and results in bond distance

information different than that obtained for other Tc(I) nitrosyl complexes. Crystal data for $C_{19}H_{21}N_6OCl_2Tc$: monoclinic space group C2/c, a=19.182(1) Å, b=10.8725(8) Å, c=11.9371(8) Å, β=116.580(7) °, V=2226.5(6) $Å^3$ to give Z=4 and R=0.025.

Chapter 3. Substitution reactions of $[Tc(NO)Cl_2(PPh_3)_2(NCCH_3)]$ with the π-acceptor ligands carbon monoxide and *tert*-butylisonitrile are reported. The labile acetonitrile ligand of $[Tc(NO)X_2(PPh_3)_2(NCCH_3)]$ (X is Cl or Br) was selectively displaced by carbon monoxide (CO) to form $[Tc(NO)X_2(PPh_3)_2(CO)]$; a disordered single crystal X-ray structure determination of the bromine analog indicates a *trans* configuration of the triphenylphosphine ligands and a *cis* orientation of the carbonyl and nitrosyl groups. The neutral ligands of $[Tc(NO)Cl_2(PPh_3)_2(CO)]$ are labile and can be displaced by pyridine to form $[Tc(NO)Cl_2(py)_3]$. The reactions of $[Tc(NO)Cl_2(PPh_3)_2(NCCH_3)]$ with *tert*-butylisonitrile (CNtBu) are analogous to those of the starting material with pyridine and yield the technetium(I) products $[Tc(NO)Cl_2(PPh_3)_2(CNtBu)]$, $[Tc(NO)Cl_2(PPh_3)(CNtBu)_2]$, or $[Tc(NO)Cl_2(CNtBu)_3]$. The bromine analog $[Tc(NO)Br_2(CNtBu)_3]$ was also synthesized for comparison with the known complex *mer, trans*-$[Tc(NO)Br_2(CNtBu)_3]$. All of the π-acid derivatives were characterized by elemental analysis, mass spectrometry, infrared, ^1H and ^{99}Tc-NMR spectroscopy.

Chapter 4. The starting material $[Tc(NO)Cl_2(PPh_3)_2(NCCH_3)]$ reacts with the monoanionic bidentate thiolate ligands alkyl xanthate and 2-mercapto-pyridine (LL) to form Tc(I) complexes of the types $[Tc(NO)Cl(PPh_3)_2(LL)]$ and $[Tc(NO)(PPh_3)(LL)_2]$, depending on the reaction stoichiometry. The lipophilicity of the xanthate complexes can be altered by changing the alkyl substituent at the xanthate terminus, but this does not appear to significantly affect the xanthate coordination mode or the Tc(I)-NO core. The complexes were characterized by elemental analysis, infrared and mass spectral data, as well as by ^1H and ^{99}Tc-NMR spectroscopy. A detailed analysis of the ^1H-NMR spectrum of $[Tc(NO)(PPh_3)(S_2COiBu)_2]$ is presented and gives insight into the coordination geometry of the complex.

Appendix 1. Data obtained in the characterization of the technetium(I) nitrosyl complexes by ^{99}Tc-NMR spectroscopy are summarized. The ^{99}Tc chemical shifts of the nitrosyl complexes were found downfield from those of other known technetium(I) complexes. Comparisons are made between the characterized technetium(I) complexes based on the trends observed in ^{99}Tc-NMR spectroscopy.

Thesis Supervisor: Dr. Alan Davison
Title: Professor of Chemistry

To my parents and Dan,

for all of their love and encouragement

Sonnet XXIX

When in disgrace with fortune and men's eyes,
I all alone beweep my outcast state,
And trouble deaf Heaven with my bootless cries,
And look upon myself, and curse my fate,
Wishing me like to one more rich in hope,
Featur'd like him, like him with friends possess'd,
Desiring this man's art, and that man's scope,
With what I most enjoy contented least;
Yet in these thoughts myself almost despising,
Haply I think on thee,- and then my state
(Like to the lark at break of day arising
From sullen earth) sings hymns at heaven's gate;

For thy sweet love remember'd such wealth brings,
That then I scorn to change my state with kings.

William Shakespeare

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INTRODUCTION

The study of nitric oxide (NO) in chemical[1] and biological[2] systems has grown tremendously in recent years. Much of this interest has been fueled by discoveries made concerning the many physiological roles of NO, which are now known to include involvement in learning and memory,[3,4] vascular relaxation,[5,6] neurotransmission,[7,8] immune response,[9,10] and signalling in the central nervous system.[11] Medical treatments of respiratory distress[12] and male impotence,[13] in particular, have been directly impacted by these discoveries, and additional advances in NO-related therapies are anticipated as understanding of nitric oxide chemistry grows.

The high degree of toxicity and the reactivity associated with the radical nitric oxide molecule suggest that in vivo NO transport is achieved through metal ion complexation. Hence, one emphasis of current nitric oxide research is the development of metal-nitrosyl pharmaceuticals capable of selective NO release. Sodium nitroprusside, $Na_2[Fe(NO)(CN)_5]$, has long been used in this capacity to effect vascular relaxation. While other metal complexes, most notably $[Ru(NO)(NH_3)_5]Cl_2$, $K_2[Ru(NO)Cl_5]$, and $K[Ir(NO)Br_5]$, have shown similar biological activity,[14] work continues in search of metal-nitrosyl complexes with greater selectivity and lower toxicity.

Due to the ideal decay properties of the metastable isotope of technetium (^{99m}Tc, $t_{1/2} = 6.0$ h, $\gamma = 143$ keV) for use in nuclear medicine, the development of ^{99m}Tc-NO radiopharmaceuticals would provide additional diagnostic capabilities not available in complexes of many other transition metals.[15] Investigations of nitrosyl complexes such as $[Tc(NO)Cl(PP)_2]^+$ [PP is 1,3-bis(dimethylphosphino)-2,2-di(methoxymethyl)propane][16,17] and n-$Bu_4N[Tc(NO)Cl_4]$[18] for potential use in myocardial perfusion imaging have been reported recently. In addition to the applications in nuclear medicine, the results of such biodistribution studies may also help elucidate the role of metal-nitrosyls in enzymatic processes.[19]

Along with their implied biological relevance, interest in both the structure and bonding of metal-nitrosyl complexes and their potential use in homogeneous catalysis[20-23] has contributed to the wealth of coordination chemistry established for NO complexes of rhenium, ruthenium, tungsten, iron, osmium, and molybdenum. By comparison, the chemistry of technetium nitrosyls is still largely unexplored. To date, less than twenty nitrosyltechnetium coordination compounds[24,25] have been characterized. The observed infrared nitrosyl stretches and the starting materials from which the complexes were prepared are listed in **Table i-1**, below.

Table i-1. Reported Technetium Nitrosyl Coordination Complexes.

Complex	ν (NO)[A]	Starting Material	Reference
Technetium(I):			
$Tc(NO)(PPh_3)_3(H)_2$	1636	$Tc(NO)Cl_3(PPh_3)_2$	26
$[Tc(NO)(NH_3)_4H_2O]^{2+}$	1680	$[TcCl_6]^{2-}$	27-29
$Tc(NO)Br_2(py)_3$	1685	$[Tc(NO)Br_4]^-$	30
$[Tc(NO)(NCS)_5]^{3-}$	1690	$[Tc(NO)(NCS)_5]^{2-}$	31
$[Tc(NO)(NH_3)(phen)_2]^{2+}$	1715	$[TcO_4]^-$, $[TcCl_6]^{2-}$	28,32
$Tc(NO)Br_2(CNCMe_3)_3$	1755	$[Tc(NO)Br_4]^-$	33
$[Tc(NO)(CNCMe_3)_5]^{2+}$	1865	$[Tc(CNCMe_3)_6]^+$	33
$[Tc(NO)Cl(PP)_2]^+$ [B]	C	$[TcO_4]^-$	16
$[Tc(NO)Cl(phen)_2]^+$	C	$[TcO_4]^-$	17,34

Table i-1, cont. Reported Technetium Nitrosyl Coordination Complexes.

Complex	ν (NO)	Starting Material	Reference
Technetium(II):			
$[Tc(NO)Cl_3(acac)]^{-}$ [D]	1770	$[Tc(NO)Cl_4]^-$	35,36
$Tc(NO)Cl_3(Me_2PhP)_2$	1770, 1795	$TcCl_3(Me_2PhP)_3$	37
$Tc(NO)Br_3(Me_2PhP)_2$	1779, 1794	$Tc(NO)Cl_3(Me_2PhP)_2$	38
$[Tc(NO)(NCS)_5]^{2-}$	1785	$[Tc(NO)Br_4]^-$	31
$[Tc(NO)Br_4]^-$	1795	$TcO_2{\cdot}xH_2O$	31
$[Tc(NO)Cl_4L]^{-}$ [E]	1795 (1805)	$[TcO_4]^-$, $[TcOCl_4]^-$, $[Tc(NO)Br_4]^-$	18,30,39
$Tc(NO)Cl_3(PPh_3)_2$	1805	$TcCl_3(PPh_3)_2(NCCH_3)$	40
$[Tc(NO)(NH_3)_4H_2O]^{3+}$	1830	$[Tc(NO)(NH_3)_4H_2O]^{2+}$	28
Technetium(III):			
$Tc(NO)Cl(SC_6HMe_4)_3$	1798	$[Tc(NO)Cl_4]^-$	41

A. Spectra were obtained in KBr and are reported in cm^{-1}.
B. PP is 1,3-bis(dimethylphosphino)-2,2-di(methoxymethyl)propane.
C. Spectroscopic data are not available for these complexes.
D. Acac is acetylacetonato.
E. L is MeOH or H_2O, depending on the solution conditions.

All of the reported complexes contain nitrosyl groups in the linear, NO^+ binding mode, and most have octahedral coordination geometries. The strong π-acid nature of the nitrosyl moiety and its ability to stabilize low oxidation states are evident in the nitrosyl derivatives. The Tc oxidation states range from (I) to (III) in these complexes and generally correlate with the types of ligands present in the technetium coordination sphere.

The Tc(I) oxidation state is stabilized by π-acid ligands. Only two nitrosyl complexes of *tert*-butylisonitrile have been reported, $[Tc(NO)(CNCMe_3)_5](PF_6)_2$ and $[Tc(NO)Br_2(CNCMe_3)_3]$.[33] In addition to π-acceptors, nitrogen donor ligands such as 1,10-phenanthroline, pyridine, and ammonia are also commonly found in Tc(I) nitrosyl complexes. Included in this group is Eakins' pink complex,[27] *trans*-$[Tc(NO)(NH_3)_4H_2O]Cl_2$, which was originally formulated as $[Tc(NH_2OH)_2(NH_3)_3H_2O]Cl_2$ but was subsequently identified as the first synthesized nitrosyltechnetium complex following additional studies[28] which included an X-ray structure determination.[29]

Nitrosyl complexes of technetium(II) tend to possess ligation by phosphines and halides. Much interest has focused on the synthesis and ESR studies of $[Tc(NO)X_4]^-$ (X is Cl[18,30,42], Br[31], or I[43]) and $[Tc(NO)X_3(PPhL_2)_2]$ (X is Cl, L is Ph[40]; X is Cl or Br, L is Me[37,38]). The nitrosyltetrachlorotechnetate ion, in particular, has proven to be a convenient starting material for the synthesis of a number of nitrosyl derivatives. The report of a simplified preparation of $[Tc(NO)Cl_4]^-$ has renewed interest in this starting material and enabled additional complexes to be synthesized via ligand exchange, including $[Tc^{II}(NO)Cl_3(acac)]^-$ and $[Tc^{III}(NO)Cl(SC_6HMe_4)_3]$.[35,36,41]

The five-coordinate thiolate derivative $[Tc^{III}(NO)Cl(SC_6HMe_4)_3]$ is the only reported[41] nitrosyl complex of technetium in the +3 oxidation state. Hence, it is not yet known if non-sulfur containing ligands can stabilize the nitrosyltechnetium(III) core.

This work presents the preparation of a new mixed ligand technetium(I) nitrosyl starting material which is suitable for selective ligand exchange. Reactions with aromatic amines, π-acceptors, and anionic sulfur ligands were performed to explore its utility as compared to n-$Bu_4N[Tc(NO)Cl_4]$ in the synthesis of low valent Tc-NO complexes. A number of new technetium(I) nitrosyl derivatives were prepared and characterized, adding to the small library of known technetium nitrosyl compounds. Data obtained in the analysis of these new complexes by ^{99}Tc-NMR spectroscopy are the first reported for technetium(I) nitrosyl complexes and provide an interesting contrast to the known ^{99}Tc chemical shifts of Tc(I) carbonyl and isonitrile derivatives.

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CHAPTER I

The Synthesis and Characterization of Mixed Ligand Technetium(I) Nitrosyl Complexes: The Preparation of Solvate Complexes from $n\text{-}Bu_4N[Tc(NO)Cl_4]$

Introduction

As interest in technetium nitrosyl compounds continues to grow, the need arises to find a convenient route into the synthesis of low valent, mixed ligand nitrosyltechnetium(I) complexes. The advantages in using this technetium nitrosyl core in studies which aim toward eventual use in nuclear medicine[1] include its diamagnetic nature and hence its ability to provide useful ^{1}H and ^{99}Tc nuclear magnetic resonance data. Numerous nitrosyltechnetium(I) complexes have been synthesized to date.[2-8] However, with the possible exception of the hydride complex $[(H)_2Tc(NO)(PPh_3)_3]$,[3] very few have shown promise as suitable starting materials for ligand substitution chemistry. For instance, "Eakin's pink compound", $[Tc^{I}(NH_3)_4(H_2O)NO]^{2+}$, was shown to be totally inert to substitution with ligands such as isonicotinamide, CO, NO, SO_2, or HS^-.[7,8]

Mixed ligand solvate complexes are common in the technetium and rhenium literature[9-13] and often serve as useful synthetic reagents. Pearlstein, for example, reports[10] that the acetonitrile solvate complex $[TcCl_3(PPh_3)_2(NCCH_3)]$, formed from a reaction between n-$Bu_4N[TcOCl_4]$ and excess triphenylphosphine in acetonitrile, undergoes displacement of the acetonitrile ligand by carbon monoxide or nitric oxide to form $[TcCl_3(PPh_3)_2(CO)]$ or $[TcCl_3(PPh_3)_2(NO)]$, respectively. While studying the chemistry of a nitrosyltechnetium system of similar composition, Roseberry noted[14] that the nitrosyltetrachlorotechnetate ion, $[Tc(NO)Cl_4]^-$, reacted with triphenylphosphine in acetonitrile to give an unidentified yellow-orange material. We now report the identification of this compound as $[Tc^{I}(NO)Cl_2(PPh_3)_2(NCCH_3)]$; the preparation and characterization of this complex and two additional nitrosyltechnetium(I) solvate complexes are presented herein. Data obtained from the analysis of $[Tc(NO)Cl_2(PPh_3)_2(NCCH_3)]$ by proton nuclear magnetic resonance spectroscopy, in particular, indicate that this complex may indeed be a suitable starting material for the synthesis of mixed ligand nitrosyltechnetium(I) complexes.

Experimental Section

Caution: Technetium-99 is a weak β^- emitter (E=292 keV, $t_{1/2}$= 2.12 x 10^5 years). All manipulations of solutions and solids were performed in laboratories approved for the use of low-level radioactivity, following precautions detailed elsewhere.[15]

Ammonium pertechnetate was obtained as a gift from DuPont Merck Pharmaceutical Company. The starting material, n-$Bu_4N[Tc(NO)Cl_4]$, was prepared by the literature method.[16] The rhenium complex $[Re(NO)Cl_2(PPh_3)_2(NCCH_3)]$, used in NMR studies, was prepared as described by Adams et al.[17] Triphenylphosphine (PPh_3) was obtained from Aldrich Chemical Company. Solvents were of at least reagent grade; solvents and reagents were used as received unless otherwise indicated. Column chromatography was performed with ICN Biomedicals Alumina N, Activity I.

Fast atom bombardment mass spectra (FABMS) were recorded with a MAT 731 mass spectrometer equipped with an Ion Tech B11N FAB gun that produced a beam of 6-8 keV Xenon neutrals. The samples were dissolved in a *p*-nitrobenzyl alcohol matrix. Peaks resulting from the most abundant isotope of chlorine, ^{35}Cl, are referenced in the mass spectra. Routine infrared spectra were recorded on a Mattson Cygnus 100 FT spectrophotometer or on a Perkin-Elmer 1600 Series FTIR. ^1H and ^{99}Tc NMR spectra were recorded at room temperature using a Varian XL-300 MHz spectrometer. The primary reference for ^{99}Tc-NMR, $[NH_4][^{99}TcO_4]$ in D_2O, resonates at 67.516 MHz and is designated as 0 ppm. A 34-μs pulse width (90° tip) and 0.15-s acquisition time were used. No additional relaxation delay was employed. For differences greater than the maximum spectral width (10^5 Hz, 1480 ppm) obtainable, chemical shifts could be calculated based on the spectrometer frequency, transmitter offset, transmitter base offset, and relative shift within the spectral window. We estimate that the error associated with these values is ±2 ppm. The presence of spectral folding or other artifacts was ruled out by changing the transmitter offset by a known frequency and verifying that the resonance moved within the spectral window by the appropriate amount and in the expected direction.[18] ESR spectra were recorded in the X-band (ν=9.41 GHz) on a Bruker ESP 300 ESR spectrometer. Magnetic susceptibility studies were performed on a Cahn Model 7500 electrobalance at 25 °C. Elemental analyses were performed by Atlantic Microlab Inc., Norcross, GA.

Preparation of [dichloromethanolnitrosylbis(triphenylphosphine) technetium(I)], [$Tc(NO)Cl_2(PPh_3)_2(HOCH_3)$] [1].

Triphenylphosphine (292.2 mg, 1.12 mmol) was added to a solution of n-$Bu_4N[Tc(NO)Cl_4]$ (47.1 mg, 0.092 mmol) in methanol (5 mL). The mixture was refluxed for three hours, during which time the solution darkened to an olive green color and an orange-pink solid precipitated. The product was collected by filtration onto a fritted glass funnel, rinsed with diethyl ether (20 mL), and dried in vacuo. Yield 39.0 mg (56.1%). The complex is soluble in dichloromethane and chloroform but slowly decomposes over time. It is slightly soluble in benzene and methanol, insoluble in diethyl ether, hexane, pentane, and water, and it reacts with many coordinating solvents.

Anal. Calcd for $C_{37}H_{34}Cl_2NO_2P_2Tc$: C, 58.73; H, 4.50; Cl, 9.39; N, 1.85.

Found: C, 58.84; H, 4.61; Cl, 8.91; N, 1.68.

FABMS(+) (m/z): 723 $[Tc(NO)Cl_2(PPh_3)_2]^+$, 688 $[Tc(NO)Cl(PPh_3)_2]^+$.

IR (KBr) (cm^{-1}): ν (NO) 1690 (vs).

ν (OH) 3505 (m).

^{1}H-NMR (CD_2Cl_2): δ=7.43 (m, 30H), 3.42 (s, 3H).

(3:1 C_6D_6/CD_3OD): δ=7.81 (m, 3H), 7.72 (m, 3H), 7.48 (m, 3H), 7.44 (m, 3H), 7.23 (m, 3H), 7.17 (m, 3H, partially obscured by C_6D_6 solvent peak), 7.09 (m, 12H), 3.24 (s, 3H).

^{99}Tc-NMR (3:1 C_6D_6/CD_3OD): δ=1665 ppm, linewidth 4590 Hz (δ TcO_4^- is 0 ppm).

(4:1 CD_2Cl_2/CD_3OD): δ=912 ppm, linewidth 2360 Hz (δ TcO_4^- is 0 ppm).

(CD_2Cl_2): δ= -614 ppm, linewidth 2230 Hz (δ TcO_4^- is 0 ppm).

The analog of **[1]** containing deuterated methanol, $[Tc(NO)Cl_2(PPh_3)_2(DOCD_3)]$, was synthesized for IR studies by substituting methanol-d_4 for MeOH as the reaction solvent.

IR (KBr) (cm^{-1}): ν (NO) 1690 (vs).

ν (OD) 2602 (m).

Preparation of [acetonitriledichloronitrosylbis(triphenylphosphine) technetium(I)], $[Tc(NO)Cl_2(PPh_3)_2(NCCH_3)]$ [2].

Method 1

Triphenylphosphine (201.7 mg, 0.77 mmol) was added to a solution of n-$Bu_4N[Tc(NO)Cl_4]$ (77.0 mg, 0.15 mmol) in acetonitrile (15 mL), and the mixture was refluxed for six hours. The solution darkened to a deep orange color, and a yellow-orange precipitate formed as the reaction progressed. After cooling to room temperature, the product was collected on a fritted glass funnel, rinsed with acetonitrile (5 mL) and diethyl ether (10 mL), and dried in vacuo. Yield 81.1 mg (70.7%). The complex is soluble in dichloromethane and chloroform but slowly decomposes over time. It is slightly soluble in benzene and methanol, insoluble in diethyl ether, hexane, pentane, and water, and it reacts with many coordinating solvents.

Anal. Calcd for $C_{38}H_{33}N_2OCl_2P_2Tc$: C, 59.61; H, 4.31; N, 3.66; Cl, 9.28.

Found: C, 59.41; H, 4.30; N, 3.77; Cl, 9.50.

FABMS(+) (*m/z*): 764 $[Tc(NO)Cl_2(PPh_3)_2(NCCH_3)]^+$, 723 $[Tc(NO)Cl_2(PPh_3)_2]^+$, 688 $[Tc(NO)Cl(PPh_3)_2]^+$.

IR (KBr) (cm^{-1}): ν (NO) 1721 (vs) and 1730 (sh).

^{1}H-NMR (CD_2Cl_2): δ=7.88 (m, 12H), 7.44 (m, 18H), 1.97 (s, 0.45H), 1.37 (s, 2.55H).

^{99}Tc-NMR (CD_2Cl_2): δ=623 ppm, linewidth 4700 Hz (δ TcO_4^- is 0 ppm).

Magnetic Susceptibility: diamagnetic in solid state

Method 2

A suspension of the pink complex **[1]** (44.3 mg, 0.059 mmol) in acetonitrile (10 mL) was stirred at room temperature overnight. With time a yellow solution was formed which yielded a yellow-orange precipitate. The precipitate was collected on a fritted glass funnel, rinsed with acetonitrile (5 mL) and diethyl ether (5 mL), and dried in vacuo. Yield 38.0 mg (85.2%).

The product was spectroscopically identical to that synthesized from Method 1.

The analog of **[2]** containing deuterated acetonitrile, $[Tc(NO)Cl_2(PPh_3)_2(NCCD_3)]$, was synthesized during an NMR study by dissolving approximately 5 mg of **[2]** in a 4 CD_2Cl_2/1 CD_3CN mixture. After one hour in solution, excess ether was added to cause the precipitation of a small amount of yellow-orange solid. The solution was removed and the solid was analyzed by mass spectrometry for evidence of uptake of the acetonitrile isotopic label.

FABMS(+) (*m/z*): 769 $[Tc(NO)Cl_2(PPh_3)_2(NCCD_3) + H]^+$, 732 $[Tc(NO)Cl(PPh_3)_2(NCCD_3)]^+$, 723 $[Tc(NO)Cl_2(PPh_3)_2]^+$, 688 $[Tc(NO)Cl(PPh_3)_2]^+$.

Attempted reaction of n-$Bu_4N[Tc(NO)Cl_4]$ with PPh_3 in pyridine.

A mixture of n-$Bu_4N[Tc(NO)Cl_4]$ (48.7 mg, 0.095 mmol) and triphenylphosphine (152.1 mg, 0.58 mmol) in pyridine (10 mL) was refluxed for four hours to form a cherry-red solution. The sample was concentrated to 1 mL by rotary evaporation and chromatographed on an alumina column conditioned with dichloromethane. The column was washed with dichloromethane (75 mL) to elute a minor orange-brown band. A red band, the major product, was eluted with acetonitrile (75 mL), while a dark brown band due to unreacted starting material remained adsorbed at the top of the column. The red fraction was dried completely by rotary evaporation then dissolved in a minimum amount of chloroform (2 mL). Addition of excess hexane (20 mL) and agitation resulted in the precipitation of a cherry-red solid. The precipitate was collected on a fritted glass funnel, rinsed with pentane (5 mL), and dried in vacuo. Yield 16.6 mg (40.0%) of $[Tc(NO)Cl_2(py)_3]$.

The product is spectroscopically identical to the material obtained below in the straightforward preparation of $[Tc(NO)Cl_2(py)_3]$.

Preparation of [dichloronitrosyltripyridinetechnetium(I)], $[Tc(NO)Cl_2(py)_3]$[19] [3].

A solution of $n\text{-}Bu_4N[Tc(NO)Cl_4]$ (38.8 mg, 0.075 mmol) in pyridine (10 mL) was refluxed overnight. The resulting cherry-red solution was concentrated to 1 mL and chromatographed on an alumina column conditioned with chloroform. The column was washed with 100 mL of 20% (v/v) dichloromethane/chloroform, and the pink-red band was eluted with 50% (v/v) dichloromethane/ acetonitrile. The pink-red fraction was dried completely to form a red residue, which was then dissolved in chloroform (4 mL). Addition of excess hexane and agitation resulted in the precipitation of a cherry red solid. The product was collected on a fritted glass funnel, rinsed with pentane (10 mL), and dried in vacuo. Yield 16.9 mg (51.6 %).

Anal. Calcd for $C_{15}H_{15}Cl_2N_4OTc$: C, 41.19; H, 3.43; Cl, 16.25; N, 12.81.

Found: C, 41.22; H, 3.46; Cl, 16.31; N, 12.77.

FABMS(+) (*m/z*): 436 $[Tc(NO)Cl_2(py)_3]^+$, 401 $[Tc(NO)Cl(py)_3]^+$, 357 $[Tc(NO)Cl_2(py)_2]^+$, 327 $[TcCl_2(py)_2]^+$, 322 $[Tc(NO)Cl(py)_2]^+$.

IR (KBr) (cm^{-1}): ν (NO) 1688 (vs).

^{1}H-NMR (CD_2Cl_2): δ=8.69 (d, 4H), 8.44 (d, 2H), 7.74 (m, 3H), 7.30 (m, 6H).

^{99}Tc-NMR (CD_2Cl_2): δ=2160 ppm, linewidth 1860 Hz (δ TcO_4^- is 0 ppm).

Attempted reaction of n-$Bu_4N[Tc(NO)Cl_4]$ with PPh_3 in dimethylsulfoxide.

Excess triphenylphosphine and n-$Bu_4N[Tc(NO)Cl_4]$ were dissolved in dimethylsulfoxide (about 10 mL) and refluxed for seventy-two hours. The solution remained apple green in color during this time; in addition, no change in the location of the nitrosyl stretching vibration of n-$Bu_4N[Tc(NO)Cl_4]$ [ν (NO) 1805 cm^{-1}] was observed in the IR spectrum of the reaction mixture.

Results and Discussion

$[Tc(NO)Cl_2(PPh_3)_2(NCCH_3)]$

The reaction of $n\text{-}Bu_4N[Tc^{II}(NO)Cl_4]$ with five-fold excess triphenylphosphine in acetonitrile yields the yellow-orange, air stable product $[Tc^{I}(NO)Cl_2(PPh_3)_2(NCCH_3)]$ **[2]** in good yield (**Figure I-1**). Room temperature magnetic susceptibility measurements, performed on the yellow-orange solid using the Faraday method, confirm that the complex is diamagnetic in the solid state. The excess triphenylphosphine acts as a reducing agent[9] to cause the conversion from the paramagnetic Tc^{II} starting material to the diamagnetic Tc^{I} product.

Like its rhenium analog,[17] $[Tc(NO)Cl_2(PPh_3)_2(NCCH_3)]$ is insoluble in many solvents and is only sparingly soluble in benzene and methanol. It can be dissolved in halogenated solvents such as chloroform and dichloromethane but slow sample decomposition occurs. The process of complex decomposition is accelerated if a solid sample of **[2]** is not carefully dried before being placed in solution. Traces of water in solutions of **[2]** cause the normally yellow complex to darken to brown within an hour. After one day in solution, **[2]** further decomposes to form a purple paramagnetic species. The room temperature ESR spectrum of this purple solution reveals a 10-line pattern, indicating the presence of a paramagnetic technetium nucleus; however, this purple species was not further characterized and its identity is not known.

A solution of $[Tc(NO)Cl_2(PPh_3)_2(NCCH_3)]$ in dichloromethane can be stabilized by the addition of excess acetonitrile. Rather than simple dissolution, reactions occur upon addition of other coordinating solvents to samples of **[2]**. For example, pyridine reacts with $[Tc(NO)Cl_2(PPh_3)_2(NCCH_3)]$

to form a bright orange diamagnetic species. This behavior of $[Tc(NO)Cl_2(PPh_3)_2(NCCH_3)]$ with coordinating solvents indicates a high receptivity toward ligand substitution.

The formulation of the yellow-orange solid as $[Tc^{I}(NO)Cl_2(PPh_3)_2(NCCH_3)]$ is well supported by spectroscopic evidence as well as by a satisfactory elemental analysis. The fast atom bombardment mass spectrum of the complex (**Figure I-2**) reveals the molecular ion peak at 764 *m/z*; fragmentation peaks due to sequential loss of acetonitrile and chloride ligand are also observed at 723 and 688 *m/z*, respectively. The presence of the nitrosyl moiety is confirmed by the compound's infrared spectrum, which shows a very strong absorbance at 1721 cm^{-1} with a shoulder at 1730 cm^{-1}. A band attributable to the CN stretching vibration of the coordinated acetonitrile is not observed in the IR spectrum of **[2]**. This absorbance tends to be very weak in transition metal complexes and is not observed in the IR spectra of acetonitrile complexes similar to **[2]**, $[MCl_3(PPh_3)_2(NCCH_3)]$ (M is Tc[10] or Re[20]). A broad (4700 Hz linewidth) resonance is found at 623 ppm in the ^{99}Tc-NMR spectrum of **[2]**.

Analysis of $[Tc(NO)Cl_2(PPh_3)_2(NCCH_3)]$ using ^{1}H-NMR spectroscopy reveals equivalent *trans*-triphenylphosphine ligands. However, because of the weak nature of the CH_3CN-Tc coordination and the lability of the acetonitrile ligand, two acetonitrile peaks are observed. A singlet due to coordinated acetonitrile appears at 1.37 ppm but does not integrate to 3H (**Figure I-3**). A second singlet, located at 1.97 ppm, results from free, noncoordinated acetonitrile. As time elapses, the concentration of free CH_3CN increases as the amount of coordinated CH_3CN decreases proportionally. **Table I-1** illustrates the changes over time in the levels of free and coordinated CH_3CN as observed using ^{1}H-NMR spectroscopy. After four days, the 'decomposed' brown solution of **[2]** gives a ^1H-NMR spectrum which shows only 16.6% of CH_3CN still coordinated to the technetium metal center, with peak integrations equivalent to only 0.50H from coordinated CH_3CN versus 2.50H from free CH_3CN. Thus, this dissociation of acetonitrile from the technetium metal center leads to sample decomposition in dichloromethane solutions.

Table I-1 ^1H-NMR data from a solution of $[Tc(NO)Cl_2(PPh_3)_2(NCCH_3)]$ in CD_2Cl_2, showing the increase in concentration of free acetonitrile as time elapses.

	CH₃CN Peak Integrations	
Time (min.)	Free CH_3CN	Coordinated CH_3CN
15	0.45	2.55
80	0.54	2.46
125	0.56	2.44
4 days	2.50	0.50

Labelling studies, performed using deuterated acetonitrile, confirm the lability of the coordinated CH_3CN ligand of $[Tc(NO)Cl_2(PPh_3)_2(NCCH_3)]$. A solution of **[2]** in a 4 : 1 mixture of CD_2Cl_2 and CD_3CN, aged 15 minutes, gives a ^1H-NMR spectrum which reveals peaks from free and coordinated acetonitrile in a 2.75 : 1 ratio, respectively (**Figure I-4**). This demonstrates that 73.3% of the coordinated CH_3CN has been displaced by the CD_3CN label [(2.20H free CH_3CN observed ÷ 3.00H coord. CH_3CN in theory) x 100%]. After one hour had elapsed, the complex was isolated and analyzed by mass spectrometry. The FABMS(+) of the product, pictured in **Figure I-5**, shows a molecular ion peak at 769 *m/z* from $[Tc(NO)Cl_2(PPh_3)_2(NCCD_3) + H]^+$; no trace of the unlabelled starting material can be detected. The label can also be observed in the 732 *m/z* fragmentation peak, $[Tc(NO)Cl(PPh_3)_2(NCCD_3)]^+$.

The rhenium analog of **[2]**, $[Re(NO)Cl_2(PPh_3)_2(NCCH_3)]$, which can be synthesized[17] according to the literature method, shows different behavior in solution, and NMR studies on this complex have not yet been reported. Although the rhenium nitrosyl complex is only sparingly soluble in CD_2Cl_2, a satisfactory ^1H-NMR spectrum can be obtained and reveals only one peak at 1.77 ppm due to acetonitrile. No additional peaks from free acetonitrile are detected. Little change is observed after CD_3CN is added to a solution of $[Re(NO)Cl_2(PPh_3)_2(NCCH_3)]$ in CD_2Cl_2. After one hour, the majority of the acetonitrile is still coordinated to the rhenium metal center. Only 5.67% of the coordinated CH_3CN has exchanged with the CD_3CN label [(0.17H free CH_3CN observed ÷ 3.00H coord. CH_3CN in theory) x 100%]. Thus, the acetonitrile ligand is much less labile in the rhenium complex as compared to the technetium complex. It is anticipated that this feature will play a primary role in determining the relative ability of the two complexes to undergo ligand exchange reactions at the acetonitrile ligand coordination site.

$[Tc(NO)Cl_2(PPh_3)_2(HOCH_3)]$

The reaction of n-$Bu_4N[Tc(NO)Cl_4]$ with excess triphenylphosphine proceeds in methanol in addition to acetonitrile. In this case, the orange-pink solid $[Tc(NO)Cl_2(PPh_3)_2(HOCH_3)]$ **[1]** is isolated in 56% yield from an olive green solution. Although the results from elemental analysis confirm the presence of one molecule of methanol in the product, the fast atom bombardment mass spectrum of **[1]** shows no molecular ion peak or other methanol-containing fragments; only fragmentation peaks containing the chloride or triphenylphosphine ligands are observed, at 723 *m/z* due to $[Tc(NO)Cl_2(PPh_3)_2]^+$ and at 688 *m/z* due to additional loss of Cl^-. A solution of **[1]** in 3:1 C_6D_6/CD_3OD yields a ^{99}Tc-NMR signal of linewidth 4590 Hz located at 1665 ppm relative to the TcO_4^- standard.

The orange-pink methanol complex **[1]** shares the solubility properties of $[Tc(NO)Cl_2(PPh_3)_2(NCCH_3)]$ and similar reactivity with coordinating species. The complex is unstable in solution without added methanol. A solution of **[1]** in 3:1 C_6D_6/CD_3OD gives a ^{1}H-NMR spectrum which indicates inequivalent triphenylphosphine ligands (**Figure I-6**). Only one methanol peak, a singlet located at 3.24 ppm, is observed. The peak location and integration are consistent with one molecule of free methanol. The pentet at 3.20 ppm, located slightly upfield from the methanol singlet, is caused by the residual CD_2HOD molecules present in the added CD_3OD NMR solvent. No resonance is evident for coordinated methanol in this spectrum.

The appearance of the ^{1}H-NMR spectrum of $[Tc(NO)Cl_2(PPh_3)_2(HOCH_3)]$ (**Figure I-6**) is drastically different from the ^{1}H-NMR spectrum of $[Tc(NO)Cl_2(PPh_3)_2(NCCH_3)]$ **[2]** (**Figure I-3**). While multiplets from the equivalent *trans*-triphenylphosphine ligands of **[2]** appear at 7.88 ppm (12 H, *o*-PPh_3) and 7.44 ppm (18H, *m*-,*p*-PPh_3), the ^{1}H-NMR spectrum of **[1]** does not show this expected triphenylphosphine equivalence.

One explanation of this observation is that the methanol molecule of complex **[1]** does not coordinate to the technetium metal center in either solution or solid state, but instead is present only as a methanol of crystallization; hence, although complexes **[1]** and **[2]** are both formulated as "$Tc(NO)Cl_2(PPh_3)_2(L)$", by this explanation complex **[1]** would be more accurately described as the five coordinate species $[Tc(NO)Cl_2(PPh_3)_2]\cdot L$. The lack of a resonance for coordinated methanol in the ^1H-NMR spectrum of **[1]** and the absence of methanol-containing peaks in the mass spectrum would tend to lend credence to this explanation. However, this formulation cannot adequately explain the inequivalent phosphine ligands observed in the ^1H-NMR spectrum of **[1]**. In addition, the fast atom bombardment mass spectral evidence should be weighted against the knowledge that molecular ion peaks often have very low relative abundances or are absent entirely from the mass spectra produced using this ionization technique.[21]

A second explanation of the observed differences between the solvate complexes **[1]** and **[2]** is that they are both 18-electron complexes $[Tc(NO)Cl_2(PPh_3)_2(L)]$ in the solid state, but that the methanol complex **[1]** undergoes a geometric change when placed in solution. Evidence of methanol coordination in the solid state or in solution would lend support to this argument. While the observed ^1H-NMR spectrum of $[Tc(NO)Cl_2(PPh_3)_2(HOCH_3)]$ indicates that complexes **[1]** and **[2]** do indeed have different coordination geometries in solution, obtaining evidence of methanol coordination is more problematic.

An attempt was made to detect methanol coordination in solution. A variable temperature NMR study was performed on a solution of **[1]** in CD_2Cl_2 which had been spiked with dry CH_3OH. No additional peaks attributable to coordinated methanol were observed, even when the sample temperature was lowered to -80°C. This piece of data cannot be used to support either of the arguments described above. Although at first glance the lack of an additional methanol peak at low temperatures seems to support the formulation of **[1]** with a methanol of crystallization, a species with a coordinated methanol ligand cannot be ruled out entirely. If methanol exchanges rapidly in solution, coordination of the methanol ligand to the technetium metal center of **[1]** would not be observable on the NMR timescale, even at lower temperatures; this type of behavior in solution would preclude the use of ^{1}H-NMR spectroscopy to confirm or deny the existence of a species with methanol coordinated to the Tc metal center.

As solid samples can be used, studies utilizing infrared spectroscopy can provide the clues needed to deduce if the methanol ligand of **[1]** is actually coordinated to the Tc metal center or if it is present merely as a methanol of crystallization. The infrared spectrum of **[1]** in KBr, pictured in **Figure I-7**, shows a very strong nitrosyl stretch at 1690 cm^{-1} due to the linear nitrosyl moiety. In addition, characteristic peaks from the methanol ligand can also be observed. A peak resulting from the methanol O-H stretch is located at 3505 cm^{-1} and appears as a sharp band of medium intensity. The appearance of a sharp band indicates either the presence of an ordered, coordinated methanol or an isolated, non-hydrogen bonded species; the same vibration tends to be strong and broad in appearance and is typically located in the range of 3420 - 3250 wavenumbers if free methanol is present in a solid sample and hydrogen bonding occurs.[21]

IR studies performed on the isotopically labelled methanol complex $[Tc(NO)Cl_2(PPh_3)_2(DOCD_3)]$ show the isotopic shift expected when deuterated methanol is substituted for CH_3OH. The O-D stretching vibration is located at

2602 cm^{-1} in the infrared spectrum of $[Tc(NO)Cl_2(PPh_3)_2(DOCD_3)]$ (**Figure I-8**), a shift of 903 cm^{-1} from the O-H absorption in complex **[1]**. The band from the O-D stretching vibration also appears as a sharp peak, which indicates the lack of hydrogen-type bonding in the sample. This evidence of both a sharp peak appearance and a correct isotopic shift suggests that, in the solid state, the methanol is indeed coordinated to the technetium metal center of **[1]**.

Evidence of identical coordination geometries of the solvate complexes $[Tc(NO)Cl_2(PPh_3)_2(HOCH_3)]$ **[1]** and $[Tc(NO)Cl_2(PPh_3)_2(NCCH_3)]$ **[2]** in the solid state is also given by the successful conversion from complex **[1]** to **[2]** upon addition of acetonitrile, described below. As this is a two phase reaction and complex **[1]** is in solution only briefly, a better picture of the nature of complex **[1]** in the solid state is provided. If complex **[1]** is only five-coordinate in the solid state, as put forth in the first argument, a greater likelihood of isomer formation upon addition of acetonitrile exists. However, the material isolated in the conversion from **[1]** to **[2]** is spectroscopically identical to **[2]** and no isomers are observed. Thus, the complex $[Tc(NO)Cl_2(PPh_3)_2(HOCH_3)]$ must be completely analogous to the acetonitrile solvate complex $[Tc(NO)Cl_2(PPh_3)_2(NCCH_3)]$ and can be considered an 18-electron, six-coordinate species.

Interesting behavior of complex **[1]** in solution was noted and is described below; however, the chemistry which is occurring has not been fully elucidated at this time. When dissolved in dichloromethane alone, compound **[1]** forms an olive green solution which exhibits a ^{99}Tc-NMR signal at - 614 ppm relative to $[NH_4][^{99}TcO_4]$. Addition of methanol to this green dichloromethane solution results in a dramatic change in spectral properties. The added methanol causes the olive green solution color to change to orange, and the ^{99}Tc-NMR signal of the complex shifts downfield to + 912 ppm.

Two possible explanations can be given to account for the observed spectroscopic changes. Solvent effects may contribute to the large shift which is exhibited in the ^{99}Tc-NMR spectrum of **[1]** after methanol is added. While a similar shift occurs when the solvent is changed from 4:1 CD_2Cl_2/CD_3OD to 3:1 C_6D_6/CD_3OD, solvent sensitivity cannot account for the observed color change. However, coordination of methanol to the technetium metal center, accompanied by a corresponding change in complex geometry, would adequately explain both the change in solution color and the observed spectral differences upon addition of methanol.

Conversion from $[Tc(NO)Cl_2(PPh_3)_2(HOCH_3)]$ to $[Tc(NO)Cl_2(PPh_3)_2(NCCH_3)]$

It is possible to convert directly from the methanol complex **[1]** to the acetonitrile complex **[2]** by the addition of excess acetonitrile. When a suspension of **[1]** in acetonitrile is stirred overnight at room temperature, the yellow-orange precipitate **[2]** is formed and can be isolated in 85% yield. A similar conversion from complex **[2]** to **[1]** is not possible, presumably due to the limited solubility of **[2]** in methanol (**Figure I-9**).

Attempted reactions with dimethylsulfoxide and pyridine

In addition to acetonitrile and methanol, the reaction between n-$Bu_4N[Tc(NO)Cl_4]$ and triphenylphosphine was explored in the coordinating solvents dimethylsulfoxide and pyridine. Both of these bases have demonstrated[9] the ability to form mixed-ligand coordination complexes with technetium. However, no isolable product is obtained when DMSO is chosen as the reaction medium. After three days of continuous reflux of the starting material and triphenylphosphine in this high boiling point solvent, no color change is observed and IR spectroscopy indicates the presence of only n-$Bu_4N[Tc(NO)Cl_4]$ in the reaction mixture.

While a reaction does occur between n-$Bu_4N[Tc(NO)Cl_4]$ and excess triphenylphosphine in pyridine, the product analogous to **[1]** and **[2]**, $[Tc(NO)Cl_2(PPh_3)_2(py)]$, is not obtained from this cherry-red reaction mixture. Rather, the major product is shown to contain no phosphine in the technetium coordination sphere. Purification of the reaction mixture by column chromatography yields two species. The minor product, an orange-brown band which elutes from an alumina column with dichloromethane, was not characterized because of sample decomposition. The major product, a red band, elutes with acetonitrile and can be identified as $[Tc(NO)Cl_2(py)_3]$. Since pyridine is a stronger Lewis base as compared to triphenylphosphine and the resulting nitrosyltechnetium-nitrogen core, [Tc(NO)-N], is exceptionally stable, pyridine binds to the metal preferentially. Hence, no $[Tc(NO)Cl_2(PPh_3)_2(py)]$ is obtained from the reaction mixture when excess pyridine is present. When n-$Bu_4N[Tc(NO)Cl_4]$ reacts directly with neat pyridine in the absence of added phosphine, $[Tc(NO)Cl_2(py)_3]$ is formed in 52% yield. The reaction behavior of n-$Bu_4N[Tc(NO)Cl_4]$ and triphenylphosphine in various solvents is summarized in **Figure I-10**.

The analogous reaction of $[Tc(NO)Br_4]^-$ with excess pyridine has been described[19] previously; a similar synthesis of $[Tc(NO)Br_2(CNR)_3]$ (R is *t*-butyl) has also been reported.[5] Orvig prepared[19] $[Tc(NO)Br_2(py)_3]$ in the manner presented herein, by refluxing $Me_4N[Tc(NO)Br_4]$ in neat pyridine for twenty-four hours. Orvig's characterization of $[Tc(NO)Br_2(py)_3]$ included elemental analysis, magnetic and conductivity data, and analysis by infrared and optical spectroscopy; the experimental data obtained in the characterization of the chloro analog **[3]** is consistent with this information. In addition to data from elemental analysis and infrared spectroscopy, the investigation described here includes the analysis of $[Tc(NO)Cl_2(py)_3]$ using fast atom bombardment mass spectrometry and proton and technetium nuclear magnetic resonance spectroscopy; a single crystal X-ray structure determination of the complex was also performed. The full characterization and an alternative method of preparation of $[Tc(NO)Cl_2(py)_3]$ are described in detail in Chapter 2.

Summary

In 1989, Pearlstein synthesized[10] $[Tc^{III}Cl_3(PPh_3)_2(NCCH_3)]$ and demonstrated its utility as a synthetic reagent which, like its rhenium congener,[20,22,23] undergoes substitution of its acetonitrile and triphenylphosphine ligands.[10,24,25] Similar mixed ligand nitrosyltechnetium complexes have been prepared and characterized and are described here. The reaction of $n\text{-}Bu_4N[Tc(NO)Cl_4]$ with excess triphenylphosphine in the weakly coordinating solvents acetonitrile or methanol (L) yields the six coordinate, diamagnetic complexes $[Tc^{I}(NO)Cl_2(PPh_3)_2(L)]$ in moderate to good yields; the use of pyridine, a better Lewis base, as the solvent results in the formation of $[Tc(NO)Cl_2(py)_3]$ rather than $[Tc(NO)Cl_2(PPh_3)_2(py)]$. The acetonitrile adduct $[Tc(NO)Cl_2(PPh_3)_2(NCCH_3)]$ shows more promise as a suitable starting material as compared to the methanol adduct, in part due to its higher synthetic yield and its greater solution stability. Characterization of **[2]** in solution demonstrates that the coordinated acetonitrile solvent molecule is quite labile. Because of this observation and its structural similarity to

$[TcCl_3(PPh_3)_2(NCCH_3)]$,[10] it is anticipated that $[Tc(NO)Cl_2(PPh_3)_2(NCCH_3)]$ will have a rich substitution chemistry at the acetonitrile and triphenylphosphine coordination sites. Chapter 2 describes some reactions of **[2]** with pyridine and other aromatic amines which were performed to explore its utility as a synthetic reagent. Like $[TcCl_3(PPh_3)_2(NCCH_3)]$, the new technetium nitrosyl complex $[Tc(NO)Cl_2(PPh_3)_2(NCCH_3)]$ promises to be a useful starting material for low valent technetium chemistry.

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Figure I-1. Scheme showing the synthesis of $[Tc(NO)Cl_2(PPh_3)_2(NCCH_3)]$ **[2]** from $NH_4[TcO_4]$.

$$\mathrm{NH_4[TcO_4]} \xrightarrow[\text{2. (TBA)Cl}]{\text{1. conc. HCl}} \mathrm{TBA[TcOCl_4]}$$

$$\mathrm{TBA[TcOCl_4]} \xrightarrow[\text{MeOH}]{\mathrm{NH_2OH{\cdot}HCl}} \mathrm{TBA[Tc(NO)Cl_4]}$$

$$\mathrm{TBA[Tc(NO)Cl_4]} \xrightarrow[\Delta]{\text{xs } \mathrm{PPh_3},\ \mathrm{CH_3CN}} \mathrm{[Tc(NO)Cl_2(PPh_3)_2(NCCH_3)]}$$

yellow-orange

Figure I-2. FABMS(+) of $[Tc(NO)Cl_2(PPh_3)_2(NCCH_3)]$ **[2]**.

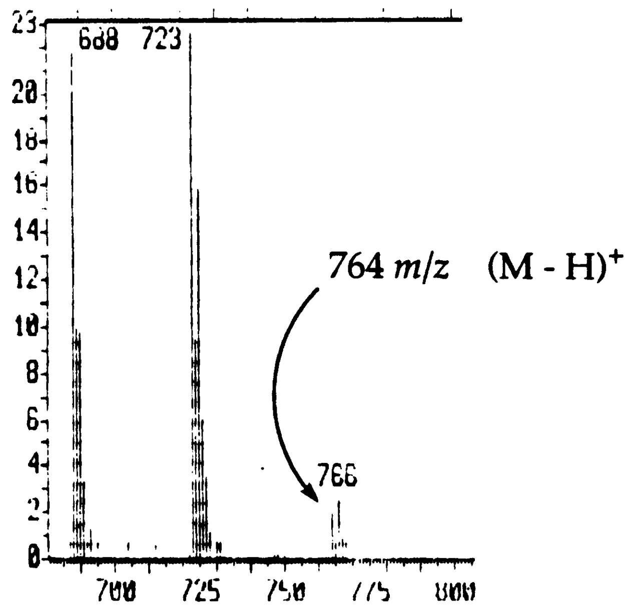

688
723
766
764 m/z (M - H)+
700
725
750
775
800

Figure I-3. ^1H-NMR spectrum of $[Tc(NO)Cl_2(PPh_3)_2(NCCH_3)]$ **[2]**, taken in CD_2Cl_2, indicating peaks from free and coordinated acetonitrile.

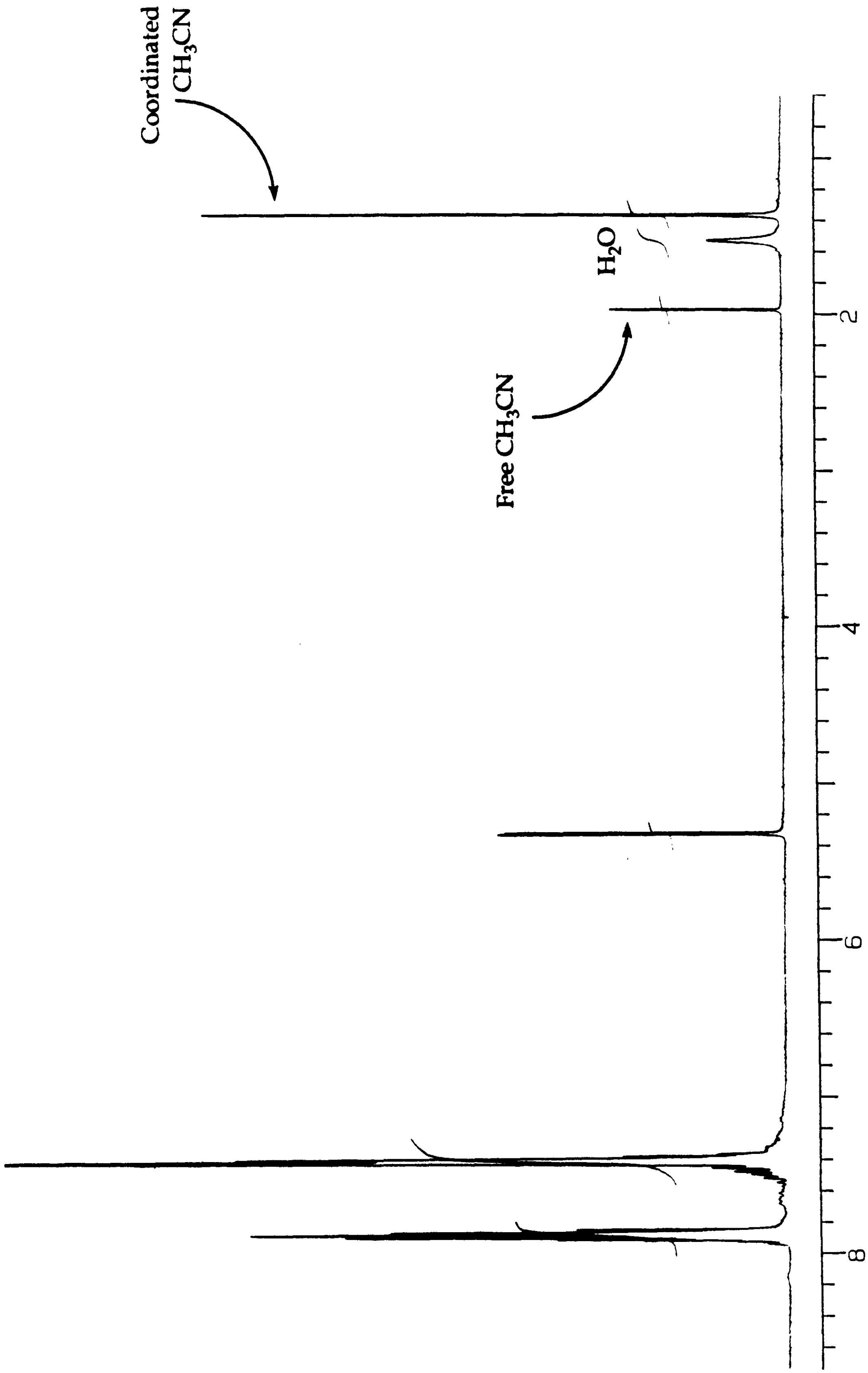
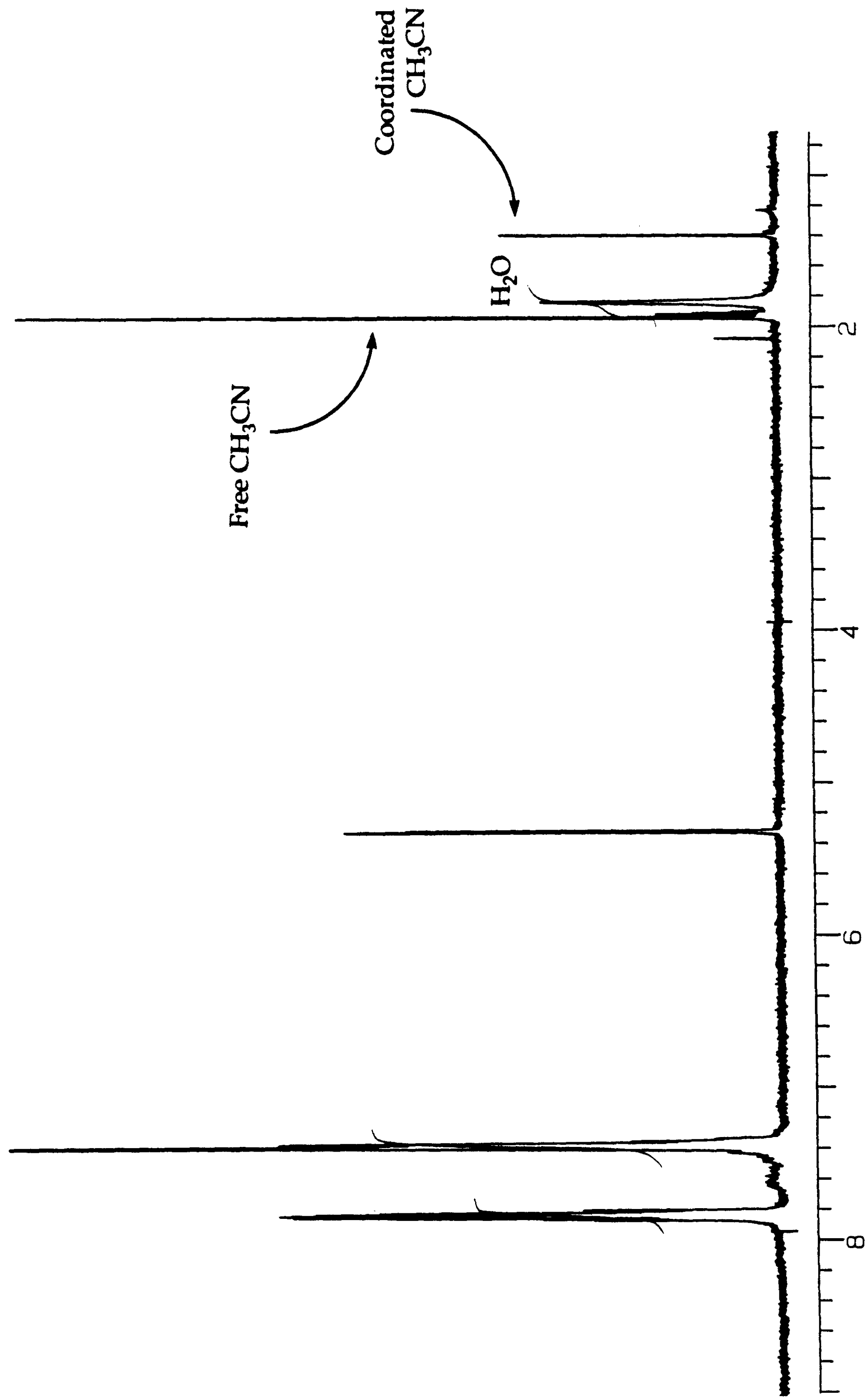

Coordinated CH3CN
H2O
Free CH3CN
2
4
6
8

Figure I-4. ^1H-NMR spectrum of $[Tc(NO)Cl_2(PPh_3)_2(NCCH_3)]$ **[2]**, taken in 4:1 CD_2Cl_2/CD_3CN, showing acetonitrile ligand exchange with CD_3CN.



Coordinated CH_3CN
H_2O
Free CH_3CN
2
4
6
8

Figure I-5. FABMS(+) of $[Tc(NO)Cl_2(PPh_3)_2(NCCD_3)]$.

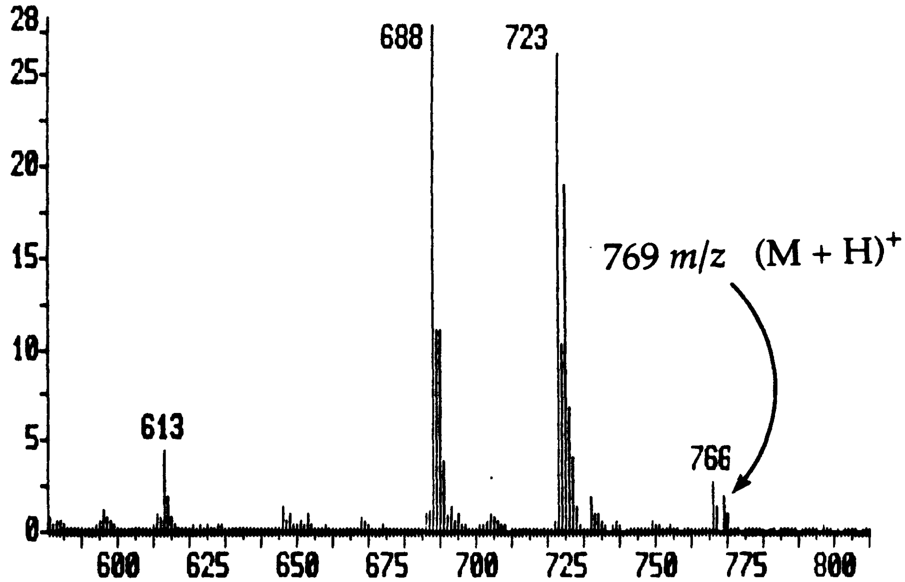

28
25
20
15
10
5
0
688
723
613
766
769 m/z (M + H)+
600
625
650
675
700
725
750
775
800

Figure I-6. ^{1}H-NMR spectrum of $[Tc(NO)Cl_2(PPh_3)_2(HOCH_3)]$ **[1]**, taken in 3:1 C_6D_6/CD_3OD.

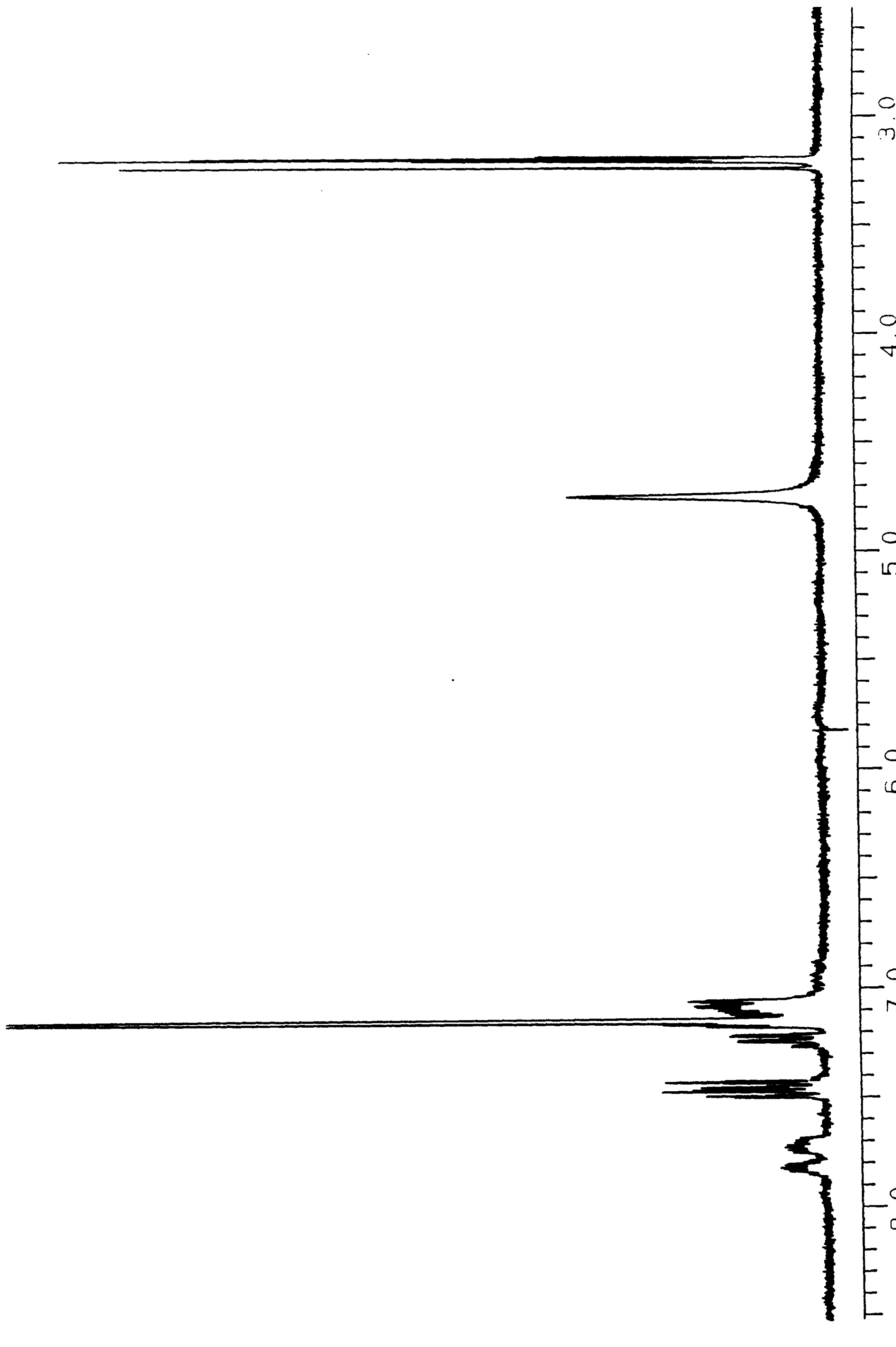
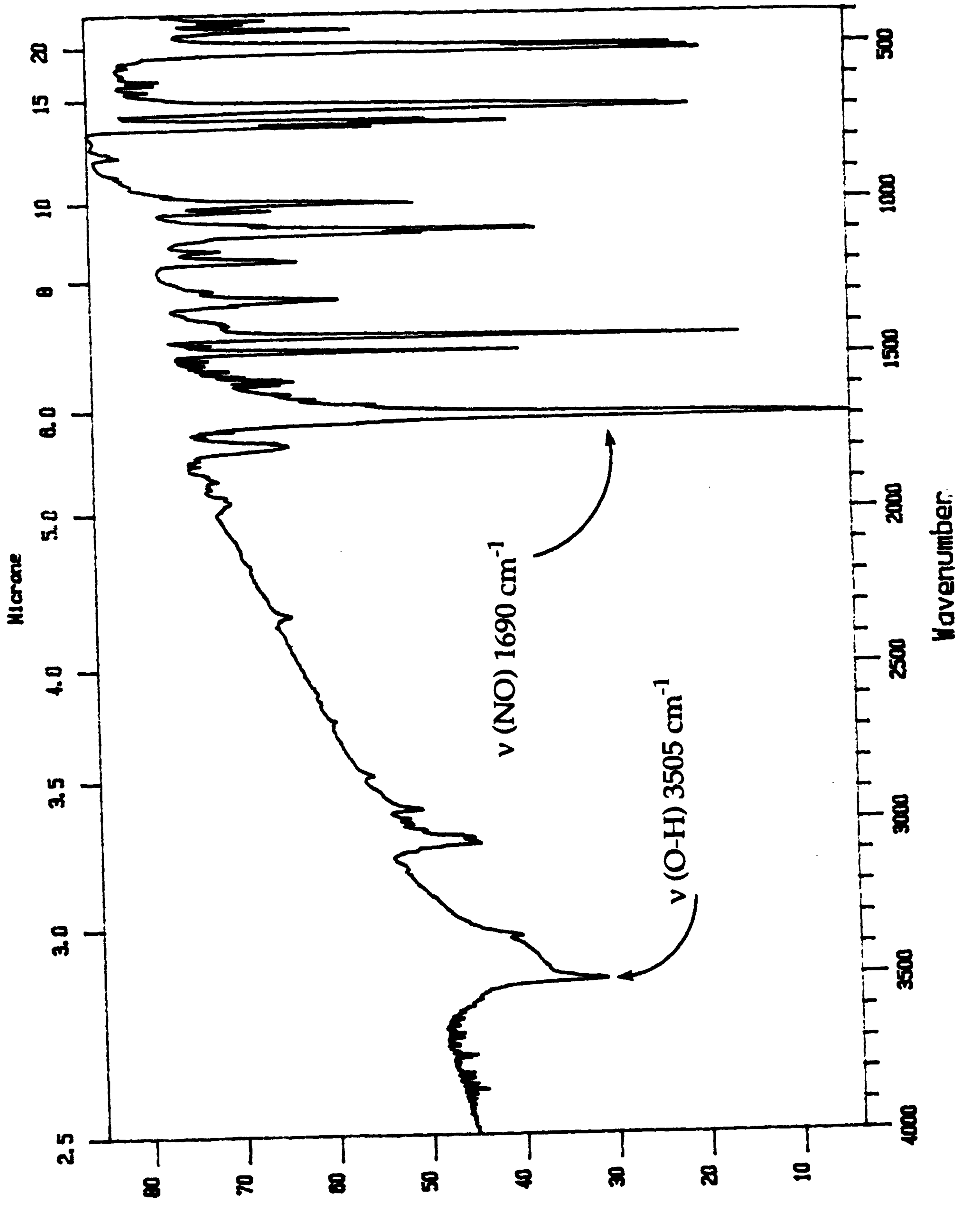
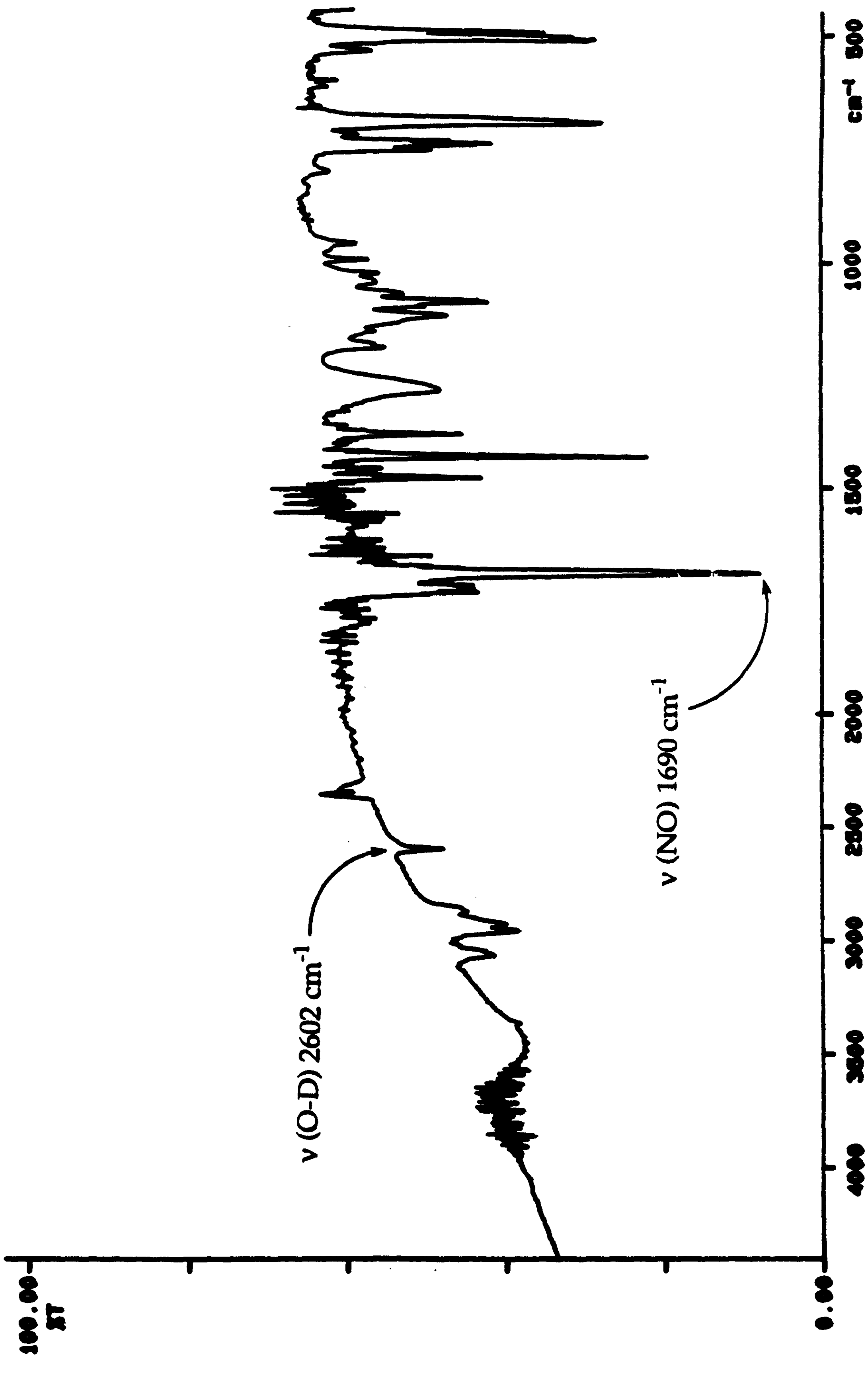

3.0
4.0
5.0
6.0
7.0
8.0

Figure I-7. Infrared spectrum of $[Tc(NO)Cl_2(PPh_3)_2(HOCH_3)]$ **[1]** (KBr).



Microns
Wavenumber
ν (NO) 1690 cm-1
ν (O-H) 3505 cm-1
2.5
3.0
3.5
4.0
5.0
6.0
8
10
15
20
4000
3500
3000
2500
2000
1500
1000
500
10
20
30
40
50
60
70
80

Figure I-8. Infrared spectrum of $[Tc(NO)Cl_2(PPh_3)_2(DOCD_3)]$ (KBr).



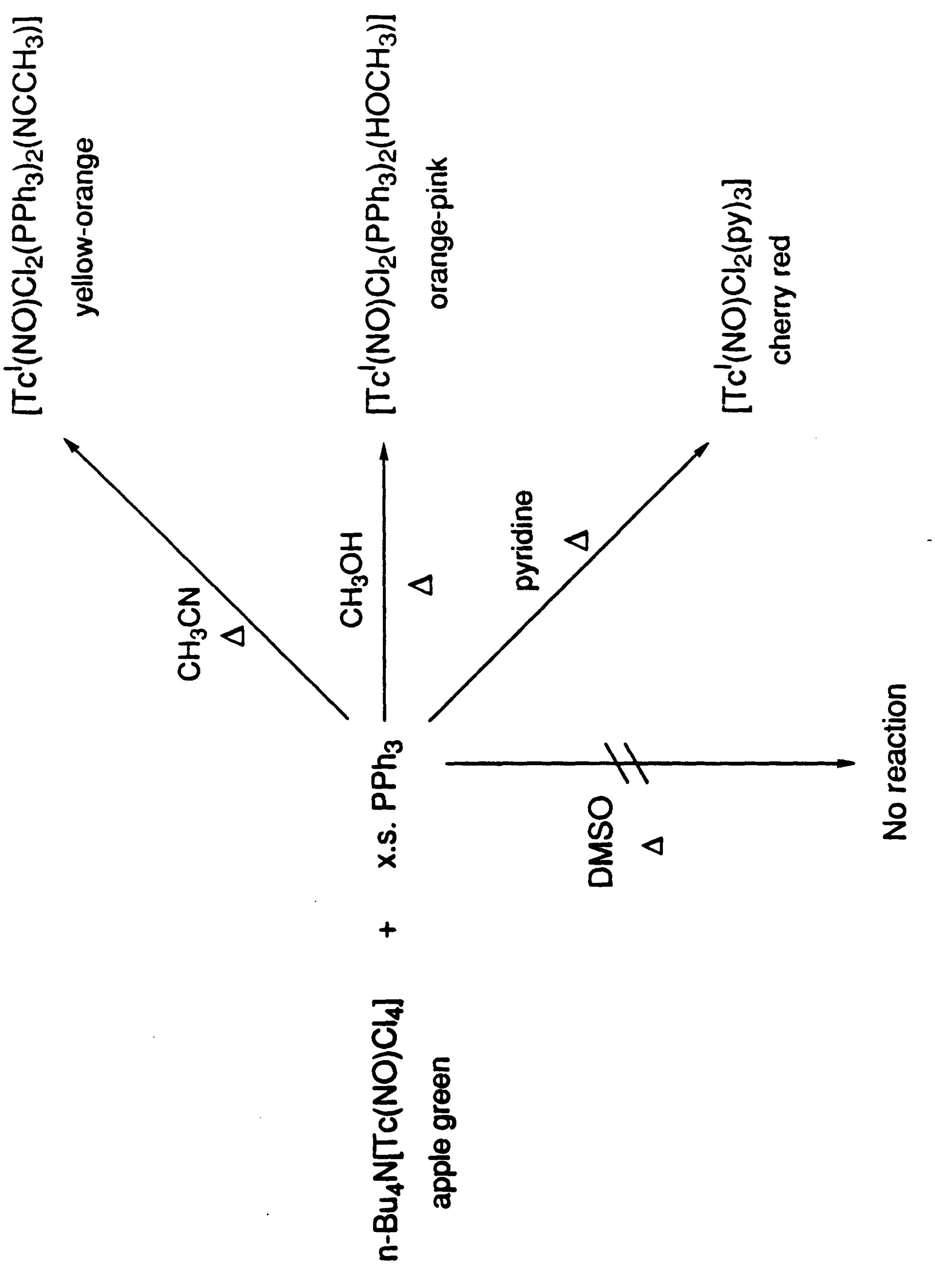
100.00
%T
0.00
4000
3500
3000
2500
2000
1500
1000
500
cm^{-1}
ν (O-D) 2602 cm^{-1}
ν (NO) 1690 cm^{-1}

Figure I-9. Scheme showing the conversion of $[Tc(NO)Cl_2(PPh_3)_2(HOCH_3)]$ **[1]** to $[Tc(NO)Cl_2(PPh_3)_2(NCCH_3)]$ **[2]** . Under similar conditions, the reverse reaction is not possible.

$$\underset{\textbf{[1]}}{[Tc^{I}(NO)Cl_2(PPh_3)_2(HOCH_3)]} + CH_3CN \xrightarrow[\text{R.T.}]{} \underset{\textbf{[2]}}{[Tc^{I}(NO)Cl_2(PPh_3)_2(NCCH_3)]}$$

$$\underset{\textbf{[2]}}{[Tc^{I}(NO)Cl_2(PPh_3)_2(NCCH_3)]} + CH_3OH \not\xrightarrow[\text{R.T.}]{} \underset{\textbf{[1]}}{[Tc^{I}(NO)Cl_2(PPh_3)_2(HOCH_3)]}$$

Figure I-10. Summary of reactions between n-$Bu_4N[Tc(NO)Cl_4]$ and excess triphenylphosphine in the coordinating solvents methanol, acetonitrile, pyridine, and dimethylsulfoxide.



n-Bu4N[Tc(NO)Cl4]
apple green
+
x.s. PPh3
CH3CN
Δ
[TcI(NO)Cl2(PPh3)2(NCCH3)]
yellow-orange
CH3OH
Δ
[TcI(NO)Cl2(PPh3)2(HOCH3)]
orange-pink
pyridine
Δ
[TcI(NO)Cl2(py)3]
cherry red
DMSO
Δ
No reaction

CHAPTER II

Substitution Reactions of $[Tc(NO)Cl_2(PPh_3)_2(NCCH_3)]$ with Aromatic Amines

Introduction

Mixed ligand phosphine complexes of technetium and rhenium have traditionally produced a rich substitution chemistry with aromatic amines. A wide variety of technetium complexes in a range of oxidation states is able to react with both pyridine and multidentate nitrogen bases. The work of Breikss[1] provides a classic example of pyridine ligand substitution chemistry. In this work, the technetium (IV) starting material $[TcCl_4(PPh_3)_2]$ is shown to react readily with pyridine to yield $[Tc^{IV}Cl_4(py)_2]$ or $[Tc^{III}Cl_3(py)_3]$, depending on the reaction conditions employed. The Tc(III) complex $[TcCl_3(PPh_3)bipy]$ can also be prepared[2] from $[TcCl_4(PPh_3)_2]$. The substitution chemistry of *mer*-$[Tc^{III}Cl_3(PMe_2Ph)_3]$[2-4] and its bromo[4] and ethyldiphenylphosphine[3,4] analogs with multidentate aromatic amines has also been reported; these reactions yield mixed ligand complexes of several types in which the amine has displaced one phosphine and one halide ligand. Recently, $[TcCl_3(PPh_3)_2(NCCH_3)]$ has also been shown[5] to be similarly reactive toward ligand exchange with 2,2'-bipyridine, 1,10-phenanthroline, and 2,2':6',2"-terpyridine.

Mixed ligand technetium nitrosyl and thionitrosyl complexes are no exceptions; they react readily with aromatic amines to form stable complexes in which the oxidation state of the technetium metal is usually found to be +1. The first such complex was isolated[6] by Armstrong and Taube in 1976 and identified as $[Tc(phen)_2NH_3(NO)]^{2+}$. The complex can be synthesized from $(NH_4)_2[TcCl_6]$ in the presence of 1,10-phenanthroline and hydroxylamine hydrochloride through a modification of the Eakins' pink[7] preparation; however, the product was not well characterized in this report. A more recent investigation[8] of the complex $[Tc(NO)NH_3(phen)_2](PF_6)_2$ yielded full characterization and a single crystal X-ray structure which shows a *cis* configuration of the phenanthroline ligands about the technetium metal center. The complexes cis-[$Tc(NX)Cl(phen)_2$]PF_6, where X is O[9] or S[8], have also been prepared and characterized.

Besides the phenanthroline complexes listed above, only one other structural type exists in which the nitrosyltechnetium core contains ligation by aromatic amines. Neutral complexes with the formulations [$Tc^I(NS)Cl_2(L)_3$][10], where L is pyridine, 4-picoline, or 3,5-lutidine, and [$Tc^I(NO)Br_2(py)_3$][11] have been reported. The thionitrosyl derivative [$Tc(NS)Cl_2(py)_3$] was prepared from a reaction of $TcNCl_4^-$ with dithionite in the presence of pyridine. Similarly, [$Tc(NO)Br_2(py)_3$] was first synthesized by refluxing n-Bu_4N[$Tc(NO)Br_4$] in neat pyridine. So far, only $(NH_4)_2$[$TcCl_6$], $TcNCl_4^-$, and n-Bu_4N[$Tc(NO)Br_4$] have served as starting materials for the synthesis of nitrosyltechnetium complexes with pyridine and related ligands. No exchange chemistry of mixed ligand phosphine nitrosyl complexes with aromatic amines has been reported.

In Chapter 1, the ability to form the mixed ligand solvate complex [$Tc(NO)Cl_2(PPh_3)_2NCCH_3$] **[2]** was demonstrated. The compound was observed to react with coordinating solvents. In addition, the coordinated acetonitrile molecule of [$Tc(NO)Cl_2(PPh_3)_2NCCH_3$] was shown to dissociate in solution and exchange with added CD_3CN. Based on these observations, it is anticipated that **[2]** will behave like [$M(NCCH_3)Cl_3(PPh_3)_2$] (M is Tc[5,12] or Re[13-15]) in exchange reactions with neutral ligands. Each compound has three ligand sites available for substitution with incoming neutral ligands; the solvent molecule and each of the two triphenylphosphine molecules can be exchanged successfully without affecting the metal oxidation state. While the ligand exchange reactions of [$Re(NCCH_3)Cl_3(PPh_3)_2$] are well documented[5,12-15] in the literature, no reaction chemistry of $[Re(NO)Cl_2(PPh_3)_2NCCH_3]$ is available for reactivity comparisons with the technetium analog **[2]**.

This chapter describes the reactions of $[Tc(NO)Cl_2(PPh_3)_2NCCH_3]$ with pyridine and multidentate aromatic amines. The ligands used in this study are pictured in **Figure II-1**. Varying the conditions in the reaction between **[2]** and nitrogen donor ligands results in a rich substitution chemistry and the formation of a variety of new technetium(I) nitrosyl complexes.

Experimental Section

Caution: Technetium-99 is a weak β^- emitter (E=292 keV, $t_{1/2}$= 2.12 x 10^5 years). All manipulations of solutions and solids were performed in laboratories approved for the use of low-level radioactivity, following precautions detailed elsewhere.[16]

Ammonium pertechnetate was obtained as a gift from DuPont Merck Pharmaceutical Company. The starting material n-$Bu_4N[Tc(NO)Cl_4]$ was prepared by the literature method[17] and complex **[2]**, $[Tc(NO)Cl_2(PPh_3)_2(NCCH_3)]$, was synthesized as described in Chapter 1. Tri(phenyl-d_5)phosphine (PPh_3-d_{15}), 3,5-dimethylpyridine (3,5-lutidine, lut), and 2,2':6',2''-terpyridine (terpy) were obtained from Aldrich Chemical Company, pyridine (py) from Mallinckrodt Specialty Chemicals Company, 2,2'-bipyridine (bipy) from Eastman Kodak Company, and 1,10-phenanthroline (phen) from Fluka Chemie AG. Solvents were of at least reagent grade; solvents and reagents were used as received unless otherwise indicated. Column chromatography was performed with ICN Biomedicals Alumina N, Activity I.

Fast atom bombardment mass spectra (FABMS) were recorded with a MAT 731 mass spectrometer equipped with an Ion Tech B11N FAB gun that produced a beam of 6-8 keV Xenon neutrals. The samples were dissolved in a *p*-nitrobenzyl alcohol matrix. Peaks resulting from the most abundant isotope of chlorine, ^{35}Cl, are referenced in the mass spectra. Routine infrared spectra were recorded on a Mattson Cygnus 100 FT spectrophotometer or on a Perkin-Elmer 1600 Series FTIR. ^1H and ^{99}Tc NMR spectra were recorded at room temperature using a Varian XL-300 MHz spectrometer. The primary reference for ^{99}Tc-NMR, $[NH_4][^{99}TcO_4]$ in D_2O, resonates at 67.516 MHz and is designated as 0 ppm. A 34-μs pulse width (90° tip) and 0.15-s acquisition time were used. No additional relaxation delay was employed. For differences greater than the maximum spectral width (10^5 Hz, 1480 ppm) obtainable, chemical shifts could be calculated based on the spectrometer frequency, transmitter offset, transmitter base offset, and relative shift within the spectral window. We estimate that the error associated with these values is ±2 ppm. The presence of spectral folding or other artifacts was ruled out by changing the transmitter offset by a known frequency and verifying that the resonance moved within the spectral window by the appropriate amount and in the expected direction.[18] Elemental analyses were performed by Atlantic Microlab Inc., Norcross, GA.

Preparation of [dichloronitrosylpyridinebis(triphenylphosphine) technetium(I)], [$Tc(NO)Cl_2(PPh_3)_2(py)$] [4].

Pyridine (0.25 mL, 3.1 mmol) was added to a suspension of compound **[2]** (22.9 mg, 0.030 mmol) in methanol (5 mL) and dichloromethane (1 mL). The mixture was stirred overnight at room temperature and remained a suspension during this time. The product was collected on a fritted glass funnel, rinsed with diethyl ether (5 mL) and hexane (5 mL), and dried in vacuo. Yield 21.0 mg (87.2%) of a pale orange solid. This complex decomposes rapidly in dichloromethane solution.

Anal. Calcd for $C_{41}H_{35}Cl_2N_2OP_2Tc$: C, 61.27; H, 4.36; Cl, 8.84; N, 3.49.

Found: C, 60.15[19]; H, 4.36; Cl, 8.96; N, 3.59.

FABMS(+) (m/z): 802 [$Tc(NO)Cl_2(PPh_3)_2(py)$]$^+$, 767 [$Tc(NO)Cl(PPh_3)_2(py)$]$^+$, 723 [$Tc(NO)Cl_2(PPh_3)_2$]$^+$, 688 [$Tc(NO)Cl(PPh_3)_2$]$^+$, 540 $[Tc(NO)Cl_2(PPh_3)(py)]^+$, 505 $[Tc(NO)Cl(PPh_3)(py)]^+$,

461 $[Tc(NO)Cl_2(PPh_3)]^+$.

IR (KBr) (cm^{-1}): ν (NO) 1703 (vs), 1685 (s).

^1H-NMR (CD_2Cl_2): δ=8.48 (s, br, 1H), 7.87 (m, 3H), 7.65 (m, 9H), 7.44 (m, 3H), 7.32 (m, 5H), 7.22 (m, 9H), 7.14 (t of t, 1H), 6.41 (d, br, 2H).

^{99}Tc-NMR (CD_2Cl_2): δ=950 and 625 ppm, linewidth 5000 Hz (δ TcO_4^- is 0 ppm).

Preparation of [dichloro(3,5-dimethylpyridine)nitrosylbis(triphenyl-phosphine)technetium(I)], $[Tc(NO)Cl_2(PPh_3)_2(lut)]$ [5].

A solution of compound **[2]** (41.4 mg, 0.054 mmol) in 3,5-lutidine (5 mL, 43.9 mmol) and methanol (1 mL) was stirred overnight at room temperature. During this time, a pale orange precipitate formed from the bright orange solution. The solid was collected on a fritted glass funnel, rinsed with diethyl ether (10 mL) and pentane (5 mL), and dried in vacuo. Yield 37.7 mg (84.0%) of $[Tc(NO)Cl_2(PPh_3)_2(lut)]\cdot H_2O$. This complex decomposes in dichloromethane solution.

Anal. Calcd for $C_{43}H_{41}Cl_2N_2O_2P_2Tc$: C, 60.78; H, 4.83; Cl, 8.36; N, 3.30.

Found: C, 60.97; H, 4.64; Cl, 8.52; N, 3.42.

FABMS(+) (*m/z*): 830 $[Tc(NO)Cl_2(PPh_3)_2(lut)]^+$, 795 $[Tc(NO)Cl(PPh_3)_2(lut)]^+$,

722 $[Tc(NO)Cl_2(PPh_3)_2 - H]^+$, 688 $[Tc(NO)Cl(PPh_3)_2]^+$,

568 $[Tc(NO)Cl_2(PPh_3)(lut)]^+$, 533 $[Tc(NO)Cl(PPh_3)(lut)]^+$.

IR (KBr) (cm^{-1}): ν (NO) 1696 (vs).

^{1}H-NMR (1:6 CD_2Cl_2/C_6D_6): δ=7.95 (m, 12H), 7.42 (s, 2H), 6.90 (m, 18 H), 6.07 (s, 1H), 1.33 (s, 6H).

^{99}Tc-NMR (CD_2Cl_2): δ=940 ppm, linewidth 4715 Hz (δ TcO_4^- is 0 ppm). A peak appears at 640 ppm as the sample decomposes.

Preparation of [dichloronitrosyldipyridine(triphenylphosphine) technetium(I)], $[Tc(NO)Cl_2(PPh_3)(py)_2]$ [6].

Method 1

A solution of compound **[2]** (27.2 mg, 0.036 mmol) in pyridine (10 mL, 123.8 mmol) was stirred at room temperature overnight. The resulting bright orange solution was flooded with excess hexane (200 mL) and refrigerated overnight to cause the precipitation of a deep orange solid. The precipitate was collected on a fritted glass funnel, rinsed with pentane (5 mL), and dried in vacuo. Yield 20.9 mg (93.6%) of $[Tc(NO)Cl_2(PPh_3)(py)_2]\cdot 0.5H_2O$.

Anal. Calcd for $C_{28}H_{26}Cl_2N_3O_{1.5}PTc$: C, 53.42; H, 4.13; Cl, 11.29; N, 6.68.

Found: C, 53.66; H, 4.09; Cl, 11.89; N, 6.28.

FABMS(+) (m/z): 619 $[Tc(NO)Cl_2(PPh_3)(py)_2]^+$, 584 $[Tc(NO)Cl(PPh_3)(py)_2]^+$, 540 $[Tc(NO)Cl_2(PPh_3)(py)]^+$, 505 $[Tc(NO)Cl(PPh_3)(py)]^+$, 461 $[Tc(NO)Cl_2(PPh_3)]^+$, 426 $[Tc(NO)Cl(PPh_3)]^+$.

IR (KBr) (cm^{-1}): ν (NO) 1696 (vs), 1706 (vs).

($CHCl_3$): ν (NO) 1708 (vs).

^{1}H-NMR (CD_2Cl_2): δ=8.65 (d, 2H), 8.38 (d, br, 2H), 7.73 (m, 7H), 7.45 (t of t, 1H), 7.31 (m, 11H), 6.86 (m, 2H).

^{99}Tc-NMR (CD_2Cl_2): δ=1379 ppm, linewidth 3000 Hz (δ TcO_4^- is 0 ppm).

Method 2

Compound **[4]** (23.2 mg, 0.030 mmol) was dissolved in pyridine (10 mL, 123.8 mmol) and stirred at room temperature overnight. The product was purified following the procedure described in Method 1. Yield 13.6 mg (73.1%).

The product was spectroscopically identical to that synthesized from Method 1.

Preparation of [acetonitriledichloronitrosylbis(tri(phenyl-d_5)phosphine) technetium(I)], $[Tc(NO)Cl_2(PPh_3\text{-}d_{15})_2(NCCH_3)]$ [7].

This compound was prepared analogously to **[2]**, substituting deuterated triphenylphosphine ($PPh_3\text{-}d_{15}$) for triphenylphosphine. Yield 143.5 mg (70.0%) of a yellow-orange solid.

FABMS(+) (*m/z*): 794 $[Tc(NO)Cl_2(PPh_3\text{-}d_{15})_2(NCCH_3)]^+$,

753 $[Tc(NO)Cl_2(PPh_3\text{-}d_{15})_2]^+$, 718 $[Tc(NO)Cl(PPh_3\text{-}d_{15})_2]^+$.

IR (KBr) (cm^{-1}): ν (NO) 1721 (vs), 1729 (sh).

^{1}H-NMR (CD_2Cl_2): δ=1.97 (s, 0.14H), 1.36 (s, 2.86H).

Preparation of [dichloronitrosyldipyridine(tri(phenyl-d_5)phosphine) technetium(I)], $[Tc(NO)Cl_2(PPh_3\text{-}d_{15})(py)_2]$ [8].

This complex was synthesized analogously to **[6]**, substituting $[Tc(NO)Cl_2(PPh_3\text{-}d_{15})_2(NCCH_3)]$ **[7]** (33.6 mg, 0.042 mmol) for **[2]**. Yield 21.6 mg (81.0%) of a bright orange solid.

FABMS(+) (m/z): 634 [$Tc(NO)Cl_2(PPh_3\text{-}d_{15})(py)_2$]$^+$, 599 [$Tc(NO)Cl(PPh_3\text{-}d_{15})(py)_2$]$^+$, 555 [$Tc(NO)Cl_2(PPh_3\text{-}d_{15})(py)$]$^+$, 520 [$Tc(NO)Cl(PPh_3\text{-}d_{15})(py)$]$^+$, 476 [$Tc(NO)Cl_2(PPh_3\text{-}d_{15})$]$^+$.

IR (KBr) (cm^{-1}): ν (NO) 1696 (vs), 1706 (vs).

($CHCl_3$): ν (NO) 1708 (vs).

^{1}H-NMR (CD_2Cl_2): δ=8.65 (m, 2H), 8.38 (d, br, 2H), 7.75 (t of t, 1H), 7.45 (t of t, 1H), 7.31 (m, 2H), 6.86 (m, 2H).

^{99}Tc-NMR (CD_2Cl_2): δ=1376 ppm, linewidth 2980 Hz (δ TcO_4^- is 0 ppm).

Preparation of [dichlorobis(3,5-dimethylpyridine)nitrosyl(triphenylphosphine)technetium(I)], [$Tc(NO)Cl_2(PPh_3)(lut)_2$] [9].

A solution of compound **[2]** (35.7 mg, 0.047 mmol) in 3,5-lutidine (10 mL, 87.8 mmol)) was stirred at room temperature overnight. The resulting bright orange solution was filtered through cotton and transferred to a 300 mL flask. The sample was flooded with excess hexane (200 mL) to form a yellow solution, which upon refrigeration yielded bright orange needles. The needles were collected on a fritted glass funnel, rinsed with pentane (10 mL), and dried in vacuo. Yield 17.7 mg (55.3%).

Anal. Calcd for $C_{32}H_{33}Cl_2N_3OPTc$: C, 56.80; H, 4.88; Cl, 10.50; N, 6.21.

Found: C, 57.09; H, 4.93; Cl, 10.35; N, 6.22.

FABMS(+) (m/z): 675 [$Tc(NO)Cl_2(PPh_3)(lut)_2$]$^+$, 640 [$Tc(NO)Cl(PPh_3)(lut)_2$]$^+$, 568 [$Tc(NO)Cl_2(PPh_3)(lut)$]$^+$, 533 [$Tc(NO)Cl(PPh_3)(lut)$]$^+$, 461 [$Tc(NO)Cl_2(PPh_3)$]$^+$, 426 [$Tc(NO)Cl(PPh_3)$]$^+$.

IR (KBr) (cm^{-1}): ν (NO) 1700 cm^{-1} (vs).

($CHCl_3$): ν (NO) 1706 (vs).

^1H-NMR (CD_2Cl_2): δ=8.29 (s, 2H), 8.00 (s, 2H), 7.71 (m, 6H), 7.30 (m, 11H), 7.03 (s, 1H), 2.24 (s, 6H), 1.95 (s, 6H).

^{99}Tc-NMR (CD_2Cl_2): δ=1382 ppm, linewidth 3600 Hz (δ TcO_4^- is 0 ppm).

Preparation of [dichlorobis(3,5-dimethylpyridine)nitrosyl(tri(phenyl-d_5) phosphine)technetium(I)], [$Tc(NO)Cl_2(PPh_3\text{-}d_{15})(lut)_2$] [10].

This complex was synthesized analogously to **[9]**, substituting [$Tc(NO)Cl_2(PPh_3\text{-}d_{15})_2(NCCH_3)$] **[7]** (15.8 mg, 0.021 mmol) for **[2]**. Yield 11.7 mg (80.6%) bright orange needles.

FABMS(+) (*m/z*): 691 [$Tc(NO)Cl_2(PPh_3\text{-}d_{15})(lut)_2 + H]^+$, 655 [$Tc(NO)Cl(PPh_3\text{-}d_{15})(lut)_2]^+$, 583 [$Tc(NO)Cl_2(PPh_3\text{-}d_{15})(lut)]^+$, 548 [$Tc(NO)Cl(PPh_3\text{-}d_{15})(lut)]^+$, 476 [$Tc(NO)Cl_2(PPh_3\text{-}d_{15})]^+$, 441 [$Tc(NO)Cl(PPh_3\text{-}d_{15})]^+$.

IR (KBr) (cm^{-1}): ν (NO) 1698 (vs), 1684 (s).

($CHCl_3$): ν (NO) 1706 (vs), 1702 (sh).

^1H-NMR (CD_2Cl_2): δ=8.28 (s, 2H), 7.99 (s, 2H), 7.36 (s, 1H), 7.02 (s, 1H), 2.29 (s, 6H), 1.94 (s, 6H).

^{99}Tc-NMR (CD_2Cl_2): δ=1383 ppm, linewidth 3850 Hz (δ TcO_4^- is 0 ppm).

Preparation of [2,2'-bipyridinedichloronitrosyl(triphenylphosphine) technetium(I)], [$Tc(NO)Cl_2(PPh_3)(bipy)$] [11].

A solution of **[2]** (25.3 mg, 0.033 mmoles) and 2,2'-bipyridine (0.038 mmoles) in chloroform (15 mL) was refluxed overnight to form a blue-green solution. After concentrating to 2 mL, excess hexane was added to cause the precipitation of a blue-green solid. The product was collected on a fritted glass funnel, rinsed with pentane (5 mL), and dried in vacuo. Yield 13.8 mg (67.6%) of $[Tc(NO)Cl_2(PPh_3)(bipy)]\cdot H_2O$.

Anal. Calcd for $C_{28}H_{25}Cl_2N_3O_2PTc$: C, 52.83; H, 3.93; Cl, 11.16; N, 6.60.

Found: C, 53.03 (52.96); H, 3.81 (3.83); Cl, 11.25; N, 6.63.

FABMS(+) (m/z): 617 $[Tc(NO)Cl_2(PPh_3)(bipy)]^+$, 582 $[Tc(NO)Cl(PPh_3)(bipy)]^+$, 546 $[Tc(NO)(PPh_3)(bipy)]^+$, 355 $[Tc(NO)Cl_2(bipy)]^+$, 320 $[Tc(NO)Cl(bipy)]^+$.

IR (KBr) (cm^{-1}): ν (NO) 1707 (vs, br).

Preparation of [dichloronitrosyl(1,10-phenanthroline)triphenylphosphine technetium(I)], $[Tc(NO)Cl_2(PPh_3)(phen)]$ [12].

A mixture of **[2]** (14.6 mg, 0.019 mmol) and excess 1,10-phenanthroline (23.3 mg, 0.13 mmol) was suspended in benzene (15 mL) and stirred at room temperature overnight to form a purple solution. The solution was concentrated to 3 mL by rotary evaporation, then diethyl ether (20 mL) was added to cause the precipitation of a dark purple solid. The product was collected on a fritted glass funnel, rinsed with diethyl ether (10 mL), and dried in vacuo. Yield 10.1 mg (80.5%) of the purple product $[Tc(NO)Cl_2(PPh_3)(phen)]\cdot H_2O$.

Anal. Calcd for $C_{30}H_{25}Cl_2N_3O_2PTc$: C, 54.55; H, 3.78; Cl, 10.75; N, 6.36.

Found: C, 54.53; H, 3.84; Cl, 10.35; N, 6.21.

FABMS(+) (m/z): 641 $[Tc(NO)Cl_2(PPh_3)(phen)]^+$,

606 $[Tc(NO)Cl(PPh_3)(phen)]^+$.

IR (KBr) (cm^{-1}): ν (NO) 1717 (s), 1730 (vs).

($CHCl_3$): ν (NO) 1718 (vs), 1711 (sh).

^{1}H-NMR (CD_2Cl_2): δ=9.37 (m, 1H), 8.44 (d of d, 1H), 8.39 (d of d, 1H), 8.00 (d, 1H), 7.90 (m, 8H), 7.48 (m, 9H), 7.34 (m, 2H).

^{99}Tc-NMR (CD_2Cl_2): δ=1477 ppm, linewidth 4960 Hz (δ TcO_4^- is 0 ppm).

Preparation of [dichloronitrosyltripyridinetechnetium(I)], [$Tc(NO)Cl_2(py)_3$] [3], by Ligand Exchange.

Method 1

A solution of compound **[2]** (31.1 mg, 0.041 mmol) in pyridine (10 mL, 123.8 mmol) was refluxed for twenty-four hours to form a cherry-red solution. After the solution volume was reduced to 1 mL under reduced pressure, the sample was chromatographed on an alumina column conditioned and washed with diethyl ether (100 mL). A gradual increase in dichloromethane concentration [20% - 50% (v/v) dichloromethane/diethyl ether] caused the elution of an orange-green band, presumably complex **[6]**. A red fraction, the major product, was eluted with acetonitrile (75 mL), filtered through cotton, and dried completely. The resulting red residue was dissolved in dichloromethane (5 mL) and layered carefully with pentane (45 mL). Red needles formed after the solution was allowed to stand at room temperature overnight. The needles were collected on a fritted glass funnel, rinsed with pentane (10 mL), and dried in vacuo. Yield 13.49 mg (75.9%). The product can be recrystallized from layered acetonitrile and diethyl ether (3 : 5 v/v) at -20 °C to form X-ray quality crystals.

Anal. Calcd for $C_{15}H_{15}Cl_2N_4OTc$: C, 41.19; H, 3.43; Cl, 16.25; N, 12.81.

Found: C, 41.22; H, 3.46; Cl, 16.31; N, 12.77.

FABMS(+) (m/z): 436 [$Tc(NO)Cl_2(py)_3$]$^+$, 401 [$Tc(NO)Cl(py)_3$]$^+$, 357 $[Tc(NO)Cl_2(py)_2]^+$, 327 $[TcCl_2(py)_2]^+$, 322 $[Tc(NO)Cl(py)_2]^+$.

IR (KBr) (cm^{-1}): ν (NO) 1688 (vs).

^{1}H-NMR (CD_2Cl_2): δ=8.69 (d, 4H), 8.44 (d, 2H), 7.74 (m, 3H), 7.30 (m, 6H).

^{99}Tc-NMR (CD_2Cl_2): δ=2160 ppm, linewidth 1860 Hz (δ TcO_4^- is 0 ppm).

Method 2

A solution of compound **[6]** (24.4 mg, 0.039 mmol) in pyridine (10 mL) was refluxed overnight to produce a cherry-red solution. The product was purified as described in Method 1. Yield 13.0 mg (76.3%).

The product was spectroscopically identical to that synthesized from Method 1.

Preparation of [dichlorotris(3,5-dimethylpyridine)nitrosyltechnetium(I)], $[Tc(NO)Cl_2(lut)_3]$ [13].

A mixture of compound **[2]** (35.1 mg, 0.046 mmol) in 3,5-lutidine (10 mL, 87.8 mmol) was refluxed overnight to form a red solution. After cooling to room temperature, the solution was transferred to a 250 mL flask and flooded with excess hexane (150 mL). A red precipitate formed immediately. This product was collected on a fritted glass funnel, rinsed with pentane (10 mL), and dried in vacuo. Yield 20.7 mg (86.4%) of $[Tc(NO)Cl_2(lut)_3]\cdot H_2O$.

Anal. Calcd for $C_{21}H_{29}Cl_2N_4O_2Tc$: C, 48.37; H, 5.18; Cl, 13.63; N, 10.75.

Found: C, 48.02; H, 5.19; Cl, 13.42; N, 10.55.

FABMS(+) (m/z): 520 $[Tc(NO)Cl_2(lut)_3]^+$, 485 $[Tc(NO)Cl(lut)_3]^+$,

413 $[Tc(NO)Cl_2(lut)_2]^+$, 383 $[TcCl_2(lut)_2]^+$, 378 $[Tc(NO)Cl(lut)_2]^+$.

IR (KBr) (cm^{-1}): ν (NO) 1686 (vs) and 1712 (m).

($CHCl_3$): ν (NO) 1701 (vs).

^{1}H-NMR (CD_2Cl_2): δ=8.31 (s, 4H), 8.03 (s, 2H), 7.34 (s, 2H), 7.32 (s, 1H), 2.26 (s, 12H), 2.20 (s, 6H).

^{99}Tc-NMR (CD_2Cl_2): δ=2197 ppm, linewidth 2730 Hz (δ TcO_4^- is 0 ppm).

Preparation of [dichloronitrosyl(2,2':6',2"-terpyridine)technetium(I)], [Tc(NO)Cl_2(terpy)] [14].

A solution of **[2]** (50.1 mg, 0.066 mmol) and 2,2':6',2"-terpyridine (25.6 mg, 0.11 mmol) in dichloromethane (10 mL) was refluxed for twenty-four hours. During the course of the reaction, the solution became dark green, and a purple precipitate began forming. The reaction mixture was cooled to room temperature, and the purple product was collected on a fritted glass funnel, rinsed with methanol (5 mL) and pentane (10 mL), and dried in vacuo. Yield 12.53 mg. Additional product was isolated from the reaction mixture in the following manner. The remaining olive solution was dried using rotary evaporation to form a dark green residue, which was dissolved in dichloromethane (10 mL) and refluxed for an additional twenty-four hours. A second crop of product precipitated and was isolated following the procedure described above. Second crop yield 8.42 mg. Total yield 20.95 mg (73.8%) of purple [Tc(NO)Cl_2(terpy)]·H_2O. The product is soluble in N,N-dimethylformamide and slightly soluble in acetone and acetonitrile. It can be recrystallized from a N,N-dimethylformamide solution layered with excess dichloromethane.

Anal. Calcd for $C_{15}H_{13}Cl_2N_4O_2Tc$: C, 39.91; H, 2.88; Cl, 15.74; N, 12.42.

Found: C, 40.27; H, 2.60; Cl, 16.24; N, 11.82.

FABMS (+) (*m/z*): 432 $[Tc(NO)Cl_2(terpy)]^+$, 397 $[Tc(NO)Cl(terpy)]^+$.

IR (KBr) (cm^{-1}): ν (NO) 1700 (vs).

^1H-NMR (DMF-d_7 one day): δ=8.51 (m, 6 H), 8.39 (t, 1 H), 7.94 (t of d, 2 H), 7.55 (t, 2 H).

^{99}Tc-NMR (DMF-d_7 one day): δ=2273 ppm, linewidth 3970 Hz (δ TcO_4^- is 0 ppm).

X-ray Crystal Structure Determination of $[Tc(NO)Cl_2(py)_3]\cdot 2CH_3CN$ [3]

Crystal data are presented in **Table II-1**. A dark red parallelepiped crystal of **[3]** was selected from a sample recrystallized from a 3:5 acetonitrile : diethyl ether solution that was cooled to -20 °C for several days. The complex crystallizes as $[Tc(NO)Cl_2(py)_3]\cdot 2CH_3CN$ and desolvates if removed from the mother liquor for extended periods of time. The crystal selected had the approximate dimensions 0.450 x 0.250 x 0.250 mm and was mounted on a glass fiber under a stream of N_2. The low temperature (-72 °C) measurements were made of an Enraf-Nonius CAD-4 diffractometer with graphite monochromated Mo $K\alpha$ radiation. The solution and refinement of the structure were performed using the TEXSAN[20] crystallographic software package. The structure was solved using Patterson methods and an absorption correction was applied. The non-hydrogen atoms were refined anisotropically.

The structure of **[3]** contained a 2-fold site disorder. The structure was solved in the space group Cc but was later refined in C2/c in order to produce bond distances which were chemically reasonable. The disordered model does give more reasonable geometric information.

Results and Discussion

Rhenium analogs of many of the nitrosyl complexes presented herein have been synthesized previously. In 1974, Adams et al. reported the preparation of $[ReCl_2(NO)(PPh_3)_2]$ from the reaction of the green benzoylazo complex $[ReCl_2(\eta_2\text{-}N_2COPh\text{-}N',O)(PPh_3)_2]$ with nitric oxide in a benzene/methanol suspension.[21] This compound adds a variety of neutral monodentate ligands (L) to produce six-coordinate complexes of rhenium(I), $[Re(NO)Cl_2(PPh_3)_2(L)]$. These complexes can be formed with ligands such as CH_3CN, py, CO, SO_2, NH_3, Ph-CN, and Ph-NC, among others. In addition, the dipyridine complex $[Re(NO)Cl_2(PPh_3)(py)_2]$ forms when $[ReCl_2(NO)(PPh_3)_2]$ is refluxed in neat pyridine. No further reaction chemistry of these adducts was reported, and the complex characterization was limited to elemental analyses, infrared spectroscopy, and magnetic susceptibility measurements. While the characterization of these six coordinate ligand adducts $[Re(NO)Cl_2(PPh_3)_2(L)]$ appeared straightforward, Adams et al. had difficulty formulating the starting material $[ReCl_2(NO)(PPh_3)_2]$ and rationalizing its observed paramagnetic moment of 1.7 μ_B.

In a subsequent reinvestigation of the system, performed[22] by Cameron et al. in 1982, this paramagnetic compound was reformulated as the methoxide complex $[Re^{II}Cl_2(OCH_3)(NO)(PPh_3)_2]$; the formulations of the Re(I) products $[Re(NO)Cl_2(PPh_3)_2(L)]$ withstood examination. Reformulation of the Adams rhenium starting material as the six-coordinate alkoxide $[ReCl_2(OCH_3)(NO)(PPh_3)_2]$ helps explain why a supposedly unsaturated complex required such long reaction times and high temperatures to achieve addition of a neutral sixth ligand.

This reformulation as a six-coordinate species also allows the comparison between the reaction chemistry of $[ReCl_2(OCH_3)(NO)(PPh_3)_2]$ and $[Tc(NO)Cl_2(PPh_3)_2(NCCH_3)]$. Both molecules can be considered as solvate complexes. Their reaction chemistry with neutral monodentate ligands is also similar, consisting of displacement of the CH_3CN or $^-OCH_3$ moieties followed by replacement of the neutral phosphine ligands. However, differences arise between the relative reactivities of $[ReCl_2(OCH_3)(NO)(PPh_3)_2]$ and $[Tc(NO)Cl_2(PPh_3)_2(NCCH_3)]$ toward either single or multiple ligand substitutions. The majority of the complexes synthesized from $[ReCl_2(OCH_3)(NO)(PPh_3)_2]$ result from substitution of the methoxide ligand only; the synthesis of $[Re(NO)Cl_2(PPh_3)(py)_2]$ is the only example presented in which multiple ligand substitution occurs. This behavior is much different than that found for the technetium solvate complex $[Tc(NO)Cl_2(PPh_3)_2(NCCH_3)]$; multiple ligand substitutions dominate the reactivity of this technetium species with pyridine and 3,5-lutidine. Unfortunately, as no reaction chemistry of $[Re(NO)Cl_2(PPh_3)_2(NCCH_3)]$ has been reported to date, a direct comparison between the reactivity of $[Re(NO)Cl_2(PPh_3)_2(NCCH_3)]$ and $[Tc(NO)Cl_2(PPh_3)_2(NCCH_3)]$ cannot be made at this time.

As summarized in **Figure II-2**, the reactions of $[Tc(NO)Cl_2(PPh_3)_2(NCCH_3)]$ with pyridine result in three new nitrosyltechnetium(I) substitution products. These are condition dependent reactions in which stepwise substitutions of the neutral ligands acetonitrile and triphenylphosphine occur. In all cases, the integrity of the nitrosyltechnetium(I) core is maintained. In the reaction of **[2]** with pyridine at room temperature, acetonitrile is the first ligand to be displaced to form the pale orange complex $[Tc(NO)Cl_2(PPh_3)_2(py)]$ **[4]**, which very easily adds another pyridine ligand to produce bright orange [Tc(NO)Cl_2(PPh_3)$(py)_2$] **[6]**. The successful displacement of all three neutral ligands can be achieved by refluxing **[2]** in pyridine to form the cherry red trispyridine complex, [Tc(NO)$Cl_2$$(py)_3$] **[3]**.

Characterization of the new technetium nitrosyl products presented in this investigation includes data from elemental analysis, fast atom bombardment mass spectrometry, infrared, and technetium and proton nuclear magnetic resonance spectroscopies. Elemental analysis and mass spectral results confirm the product compositions. The mass spectrum of each product invariably displays a molecular ion peak, with the correct chlorine isotope pattern, and a distinguishable fragmentation pattern from sequential loss of chloride or neutral ligands.

Data from the infrared spectra of the products confirm the presence of the linear NO^+ moiety in all cases. The nitrosyl absorbances are clustered between 1688 - 1725 cm^{-1}, at the low end of the range established[23] for linear nitrosyl ligands. These low absorbances occur due to strong metal to nitrosyl back bonding, which results in the corresponding decrease in strength of the [NO] bond. The linearly bonded nitrosyl ligand and the Tc(I) oxidation state are maintained in all of the ligand substitution products presented in this investigation.

[Tc(NO)Cl_2(PPh_3)$(py)_2$]

When [Tc(NO)$Cl_2$$(PPh_3)_2$($NCCH_3$)] is stirred overnight in pyridine, the bright orange complex [Tc(NO)Cl_2(PPh_3)$(py)_2$] **[6]** is formed. The mass spectrum of **[6]** shows a molecular ion peak at 619 *m/z* and assignable fragmentation patterns due to loss of chloride (584 *m/z*), pyridine (540 *m/z*), and multiple ligand losses. A very strong infrared nitrosyl stretch is located at 1708 cm^{-1} in the chloroform solution spectrum of **[6]**.

This dipyridine complex is stable in dichloromethane solution and gives a well resolved ^1H-NMR spectrum (see **Figure II-3A**). Because the pyridine proton resonances are partially obscured by the triphenylphosphine peaks, the deuterated triphenylphosphine complex **[8]** was synthesized; its ^1H-NMR spectrum is shown in **Figure II-3B**. Three pairs of pyridine proton resonances are observed in the ^1H-NMR spectrum of $[Tc(NO)Cl_2(PPh_3\text{-}d_{15})(py)_2]$. The peak locations and integrations in this spectrum are consistent with the presence of non-equivalent, *cis*-pyridine ligands in the complex **[8]**. The doublets at 8.65 and 8.38 ppm, which integrate in a 2:2 ratio, represent the α protons of the pyridine ligands. The β and γ protons resonances are located upfield, as labelled in **Figure II-3B**. Assignments were confirmed by homonuclear decoupling experiments.

The ^{99}Tc-NMR resonance of the dipyridine complex **[6]** is located at 1379 ppm, and the deuterated complex **[8]** shows a similar signal at 1376 ppm.

$[Tc(NO)Cl_2(PPh_3)_2(py)]$

An impure sample of **[6]**, produced from only partial reaction between $[Tc(NO)Cl_2(PPh_3)_2(NCCH_3)]$ and pyridine, gives a mass spectrum with peaks assignable to the monopyridine adduct, $[Tc(NO)Cl_2(PPh_3)_2(py)]$ **[4]**, amidst the sample peaks from **[6]** itself (**Figure II-4A**). The monopyridine complex **[4]** can be isolated by suspending **[2]** in a dichloromethane/methanol mixture (1:5) in the presence of a small amount of pyridine. Elemental analysis and mass spectrometry (**Figure II-4B**) confirm the formulation of the complex. The infrared spectrum of **[4]** shows two nitrosyl stretches at 1685 (s) and 1703 (vs) cm^{-1}, indicating the presence of isomers. The complex is soluble in dichloromethane and chloroform, but decomposes rapidly to form a brown diamagnetic species. Evidence of this decomposition product can be seen in the ^{99}Tc-NMR, which shows two very broad resonances at 950 and 625 ppm. The solution further decomposes over time to produce a purple paramagnetic species which was not characterized. Because of the decomposition in solution, the peaks due to the complex itself, isomers, or decomposition products cannot be differentiated in the ^{1}H-NMR spectrum of **[4]**.

$[Tc(NO)Cl_2(py)_3]$

A cherry-red compound is formed when compound **[2]** is refluxed in pyridine for twenty-four hours. The complex $[Tc(NO)Cl_2(py)_3]$ **[3]** can be separated from the reaction mixture in 76% yield using chromatographic methods. The infrared spectrum of the complex shows a low nitrosyl stretch at 1688 cm^{-1}, and the mass spectrum gives a molecular ion peak at 436 *m/z* and assignable fragmentation peaks from loss of the chloride (401 *m/z*), pyridine (357 *m/z*), and nitrosyl (327 *m/z*) ligands. A strong ^{99}Tc-NMR signal is observed at 2160 ppm.

As discussed in Chapter 1, the trisOpyridine complex **[3]** can also be synthesized directly from n-$Bu_4N[Tc(NO)Cl_4]$ in refluxing pyridine, following the method of Orvig.[11] The rhenium analog of **[3]**, $[Re^{I}(NO)Cl_2(py)_3]$, has been prepared[24] similarly from a reaction between the pentachloronitrosyl-rhenate(II) anion and pyridine in boiling diglyme.

The ^{1}H-NMR spectrum of $[Tc(NO)Cl_2(py)_3]$ is very similar to that of the thionitrosyl analog, $[Tc(NS)Cl_2(py)_3]$, synthesized[10] by Lu and Clarke; a single crystal X-ray structure of the 4-picoline (pic) derivative, $[Tc(NS)Cl_2(pic)_3]$, shows a meridional configuration of picoline ligands about the technetium metal center (**Figure II-5**). Based on a comparison of ^{1}H-NMR data between **[3]** and the thionitrosyl complexes, a meridional geometry of pyridine ligands is also indicated in $[Tc(NO)Cl_2(py)_3]$. The ^{1}H-NMR spectrum of **[3]** (**Figure II-6**) shows resonances at 8.69 and 8.44 ppm which integrate in a 4:2 ratio and are caused by the α protons of the *mer*-pyridine ligands. The signal at 8.69 ppm is due to the two mutually trans pyridines, whereas that at 8.44 ppm is from the unique pyridine ligand. The multiplets at 7.74 and 7.30 ppm are due to the coincidental overlap of all γ and β pyridine proton resonances, respectively.

X-ray Crystal Structure Determination of $[Tc(NO)Cl_2(py)_3]\cdot 2CH_3CN$ [3]

A single crystal X-ray structure determination was performed on the trispyridine complex $[Tc(NO)Cl_2(py)_3]\cdot 2CH_3CN$ to confirm the meridional pyridine ligand geometry and the linearity of the nitrosyl ligand. Atomic positional parameters are listed in **Table II-2**. The PLUTO[25] (**Figure II-7**) and ORTEP[26] (**Figure II-8**) diagrams are also pictured. Selected bond distances and angles are summarized in **Table II-3**. The unit cell of $[Tc(NO)Cl_2(py)_3]\cdot 2CH_3CN$ is monoclinic with the space group C2/c. The ligating atoms form an octahedron; the Cl1-Tc-N1 angle is linear (180.00°), and the angles Cl2-Tc-N4 and N2-Tc-N2 are nearly linear (177.2(2)° and 176.72(8)°, respectively). The L_{cis}-Tc-L_{cis} bond angles are also consistent with an octahedral geometry and range in size from 87.9° to 91.64° (**Table II-3**).

As predicted from ^{1}H-NMR data, the ORTEP diagram of **[3]** depicts a complex analogous to *mer*-$[Tc(NS)Cl_2(pic)_3]$, with the pyridine ligands arranged in a meridional configuration cis to the Tc-NO bond. **Table II-4** compares the structural data obtained for both *mer*-$[Tc(NX)Cl_2(L)_3]$ complexes. The average Tc-$N_{pyridine}$ distance of **[3]** is 2.129 Å., similar to the average length of 2.140 Å. found in the thionitrosyl derivative. Another feature common to both structures is the pinwheel orientation of the pyridine ligands around the technetium metal center; each pyridine is tilted 35 - 45° from vertical relative to the position of the Tc-NO bond. One chloride ion is located *cis* to the Tc-NO moiety; the Tc-Cl1 bond distance of 2.4319(7) Å. compares well with the reported distance of 2.430(2) Å. in *mer*-$[Tc(NS)Cl_2(pic)_3]$. However, due to the disorder present in the structure of **[3]**, problems arise when attempting to compare the structural information obtained on the Tc-Cl2 or Tc-N4-O bonds with the data derived from the thionitrosyl structure determination.

The ORTEP diagram of *mer*-$[Tc(NO)Cl_2(py)_3]\cdot 2CH_3CN$ supports the IR data and confirms that the nitrosyl moiety is present in the complex in the linear, NO^+ binding mode. However, the two-fold site disorder inherent in the system and the subsequent modelling do not allow definitive Tc^I-NO bond distances to be given. The nitrosyl and chloride groups possess a similar number of electrons and are therefore difficult to distinguish crystallographically. Problems in differentiating the two groups have been reported[27] in the literature. A site disorder, evident along the Cl2-Tc-N4-O axis, is present in the structure of *mer*-$[Tc(NO)Cl_2(py)_3]\cdot 2CH_3CN$ for this reason. Hence, the Tc-N4 bond distance of 1.781(5) Å. is longer than expected for a technetium(I) nitrosyl complex. The average Tc^I-NO bond distance is 1.727Å for the three structurally characterized nitrosyl technetium complexes.[8,28,29] The N4-O bond length of 1.192(5) Å. is also slightly longer than expected.

The system disorder becomes evident when analyzing the Tc-Cl2 bond distance as well. The Tc-Cl bond located trans to the nitrosyl group is expected to be elongated relative to the Tc-Cl bond in the cis position. In addition, the trans effect of the nitrosyl ligand is expected to be larger than that of the thionitrosyl ligand. Neither of these predictions holds true in the structure of *mer*-[$Tc(NO)Cl_2(py)_3$]·$2CH_3CN$ due to the crystallographic site disorder. The derived Tc-$Cl2_{trans}$ bond length of 2.367(2) Å is shorter than both the Tc-$Cl1_{cis}$ length (2.4319(7) Å.) found in **[3]** and the Tc-Cl_{trans} bond length (2.443(1) Å.) determined in the structure of *mer*-[$Tc(NS)Cl_2(pic)_3$]. However, despite this lack of accurate bond distances, the gross structural information obtained from this determination is useful in establishing the geometry of *mer*-[$Tc(NO)Cl_2(py)_3$] and in predicting the geometry of the related complexes presented in this investigation.

Evidence for stepwise reaction mechanism in pyridine substitution

It is possible to convert between pyridine substitution products. For example, [$Tc(NO)Cl_2(PPh_3)(py)_2$] can be formed by dissolving [$Tc(NO)Cl_2(PPh_3)_2(py)$] in pyridine. Likewise, [$Tc(NO)Cl_2(PPh_3)(py)_2$] can be refluxed in pyridine to produce [$Tc(NO)Cl_2(py)_3$]. This stepwise behavior of the ligand substitution pyridine reactions is summarized in **Figure II-2**.

Complexes with substituted pyridine ligands

In an attempt to form species which were less susceptible to decomposition in solution, analogous complexes were prepared with the bulkier pyridine ligand, 3,5-lutidine. The lutidine substituted complexes [$Tc(NO)Cl_2(PPh_3)_2(lut)$] **[5]**, [$Tc(NO)Cl_2(PPh_3)(lut)_2$] **[9]**, and [$Tc(NO)Cl_2(lut)_3$] **[13]** can be synthesized from the reaction of **[2]** with 3,5-lutidine under the various temperature conditions outlined above. The physical properties of the lutidine complexes are very similar to those of their pyridine analogs, and the sample characterization is analogous, with two exceptions. The first difference is that the ^{99}Tc-NMR signal for [$Tc(NO)Cl_2(lut)_3$] is located at 2197 ppm, thirty-seven ppm higher than the 2160 ppm signal from

$[Tc(NO)Cl_2(py)_3]$. A difference can also be noted in the relative stability of $[Tc(NO)Cl_2(PPh_3)_2(py)]$ and $[Tc(NO)Cl_2(PPh_3)_2(lut)]$ in dichloromethane solution. The monolutidine product **[5]** is slightly more stable as compared to its pyridine analog and decomposes in dichloromethane at a slower rate; this can be seen in the ^{99}Tc-NMR spectrum of **[5]**, in which only the product's signal at 940 ppm is initially observed. As the acquisition time increases and product decomposition begins to occur, a second resonance appears at 640 ppm. On the other hand, the ^{99}Tc-NMR spectrum of **[4]** displays two resonances, at 950 and 625 ppm, initially.

Complexes with multidentate aromatic amines

Complexes which are analogous to $[Tc(NO)Cl_2(PPh_3)(py)_2]$ and $[Tc(NO)Cl_2(py)_3]$ can be synthesized using the multidentate aromatic amines 2,2'-bipyridine, 1,10-phenanthroline, and 2,2':6',2"-terpyridine, pictured in **Figure II-9**. The relative ligand composition in these derivatives is confirmed by mass spectrometry and elemental analysis. As in the synthesis of **[6]**, reactions of **[2]** with the bidentate amines 2,2'-bipyridine and 1,10-phenanthroline result in the displacement of acetonitrile and one phosphine ligand, forming $[Tc(NO)Cl_2(PPh_3)(NN)]$ (NN is bipy or phen), whereas the reaction of the starting material with 2,2':6',2"-terpyridine yields $[Tc(NO)Cl_2(terpy)]$.

$[Tc(NO)Cl_2(PPh_3)(phen)]$

When 1,10-phenanthroline is chosen as the incoming ligand, the dark purple complex $[Tc(NO)Cl_2(PPh_3)(phen)]$ **[12]** is formed in 80.5% yield. The fast atom bombardment mass spectrum of **[12]** reveals a molecular ion peak at 641 *m/z* and an additional fragmentation peak at 606 *m/z* from the loss of one chloride ion. The ^{99}Tc-NMR spectrum of **[12]** shows a broad resonance (4960 Hz linewidth) located at 1477 ppm relative to TcO_4^-. A sample of the complex in KBr yields an infrared spectrum which reveals two bands of unequal intensity, located at 1717(s) and 1730(vs) wavenumbers, attributable to the nitrosyl stretching vibration. A solution spectrum, taken of the complex in chloroform, reveals a very strong band at 1718 cm^{-1} with a shoulder at 1711 cm^{-1}. Since only one nitrosyl peak is expected according to symmetry considerations, the appearance of two bands in the IR spectrum suggests the existence of isomers. This is supported by data from the ^1H-NMR spectrum of $[Tc(NO)Cl_2(PPh_3)(phen)]$, given in **Figure 10**, which clearly shows two sets of peaks from the phenanthroline protons.

Analysis of **[12]** by ^1H-NMR spectroscopy yields information about isomers of the complex. The spectrum confirms the 1:1 ratio of phenanthroline to triphenylphosphine which is expected for the complex $[Tc(NO)Cl_2(PPh_3)(phen)]$. A detailed analysis of the ^1H-NMR spectrum reveals two peaks at 8.00 ppm from the equivalent, uncoupled protons in positions 5 and 6 of 1,10-phenanthroline (inset, **Figure 10**), where only a singlet is expected based on comparisons with spectra of free 1,10-phenanthroline and of similar mixed ligand technetium complexes.[2] Protons in the 2,9 and 4,7 positions also exhibit unexpected duplicate resonances. This peak duplicity cannot be attributed merely to the presence of an inhomogeneous magnetic field around the phenanthroline ligand, since each observed set of peaks, while very similar, is not identical in size or integration values. The observed spectrum can, however, be explained if isomers of **[12]** are assumed to be present in solutions of the complex in slightly different concentrations. All attempts to separate the isomers by chromatographic methods failed.

$[Tc(NO)Cl_2(PPh_3)(bipy)]$

The 2,2'-bipyridine complex $[Tc(NO)Cl_2(PPh_3)(bipy)]$ **[11]**, synthesized in a similar fashion to **[12]**, also exhibits isomerism in solution and in the solid state. The ^{99}Tc-NMR spectrum of **[11]** typically reveals three peaks, centered at 67.566 MHz, caused by three inequivalent technetium centers. Hence, resolution and interpretation of the ^{99}Tc and ^{1}H-NMR spectra are quite difficult due to this presence of multiple isomers. As with **[12]**, analysis of samples of $[Tc(NO)Cl_2(PPh_3)(bipy)]$ by thin layer chromatography using various solvent systems showed no separation of these isomers.

The observed isomers of complexes of the type $[Tc(NO)Cl_2(PPh_3)(NN)]$ may be caused by the rigid nature of the aromatic amine ligands. As discussed above, the X-ray structure determination of *mer*-$[Tc(NO)Cl_2(py)_3]$ **[3]** reveals a 35 - 45° pitch of the pyridine rings. If this structure represents the most stable and preferred ligand orientation in complexes of this type, then the rigid multidentate bipyridine and phenanthroline molecules cannot bind in this manner because of undue strain.

$[Tc(NO)Cl_2(terpy)]$

Analysis of $[Tc(NO)Cl_2(terpy)]$ **[14]** is straightforward based on comparisons with the pyridine derivative **[3]**; the synthesis of **[14]**, however, is very low yielding. The complex is prepared by refluxing a dichloromethane solution of **[2]** and excess 2,2':6',2"-terpyridine for twenty-four hours. During this time a purple solid precipitates from the reaction mixture and represents a yield of approximately 35%. The mother liquor can be collected and refluxed for a second twenty-four hour period to double the amount of product yield. The purple solid has a limited solubility in DMF, acetonitrile, and acetone.

Summary

The mixed ligand complex $[Tc(NO)Cl_2(PPh_3)_2(NCCH_3)]$ has been shown to be a good starting material for the synthesis of low valent nitrosyl complexes with aromatic amines. Ligand exchange reactions between $[Tc(NO)Cl_2(PPh_3)_2(NCCH_3)]$ and aromatic amines such as pyridine, 3,5-lutidine, 2,2'-bipyridine, 1,10-phenanthroline, and 2,2':6',2''-terpyridine result in the successful formation of nitrosyltechnetium(I) complexes of the types $[Tc(NO)Cl_2(PPh_3)_2(N)]$, $[Tc(NO)Cl_2(PPh_3)(N)_2]$, or $[Tc(NO)Cl_2(N)_3]$, depending on the choice of incoming nitrogen base (N) and the reaction conditions employed. These are stepwise reactions in which displacement of the labile acetonitrile molecule is followed by substitution of successive phosphine ligands. Chapter 3 describes similar exchange reactions with the π-accepting ligands carbon monoxide and *tert*-butylisonitrile.

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Table II-1. X-ray Data for Structure Determination of *mer*-$[Tc(NO)Cl_2(py)_3]\cdot 2CH_3CN$.

A. Crystal Data

Empirical Formula	$C_{19}H_{21}N_6OCl_2Tc$
Formula Weight	517.32
Crystal Color, Habit	red, parallelpiped
Crystal Dimensions (mm)	0.450 X 0.250 X 0.250
Crystal System	monoclinic
No. Reflections Used for Unit Cell Determination (2θ range)	25 (12.0 - 26.0°)
Omega Scan Peak Width at Half-height	0.21
Lattice Parameters:	a = 19.182 (1)Å b = 10.8725 (8)Å c = 11.9371 (8)Å β = 116.580 (7)° V = 2226.5 (6)Å^3
Space Group	C2/c (#15)
Z value	4
D_{calc}	1.543 g/cm^3
F_{000}	1048
μ(MoKα)	8.83 cm^{-1}

Table II-1, continued. X-ray Data for Structure Determination of *mer*-$[Tc(NO)Cl_2(py)_3]\cdot 2CH_3CN$.

B. Intensity Measurements

Diffractometer	Enraf-Nonius CAD-4
Radiation	MoKα (λ = 0.71069 Å)
Temperature	-72°C
Attenuator	Zr foil, (factor = 17.9)
Detector Aperture	2.0 - 2.5 mm horizontal 2.0 mm vertical
Crystal to Detector Distance	21 cm
Scan Type	ω
Scan Rate	1.9 - 16.5°/min (in omega)
Scan Width	(0.80 + 0.35 tanθ)°
$2\theta_{max}$	54.9°
No. of Reflections Measured	Total: 2768 Unique: 2689 (R_{int} = .036)
Corrections	Lorentz-polarization Absorption (trans. factors: 0.91 - 1.14) Secondary Extinction (coefficient: 0.56346E-06)

Table II-1, continued. X-ray Data for Structure Determination of *mer*-$[Tc(NO)Cl_2(py)_3]\cdot 2CH_3CN$.

C. Structure Solution and Refinement

Structure Solution	Patterson Method
Refinement	Full-matrix least-squares
Function Minimized	$\Sigma\, w\, (\lvert Fo\rvert - \lvert Fc\rvert)^2$
Least-squares Weights	$4Fo^2/\sigma^2(Fo^2)$
p-factor	0.02
Anomalous Dispersion	All non-hydrogen atoms
No. Observations ($I>3.00\sigma(I)$)	2331
No. Variables	148
Reflection/Parameter Ratio	15.75
Residuals: R; R_w	0.025; 0.030
Goodness of Fit Indicator	1.41
Max Shift/Error in Final Cycle	0.21
Maximum Peak in Final Diff. Map	0.29 $e^-/Å^3$
Minimum Peak in Final Diff. Map	-0.39 $e^-/Å^3$

Table II-2. Atomic Positional Parameters and B(eq) for *mer*-[$Tc(NO)Cl_2(py)_3$]·$2CH_3CN$.

atom	x	y	z	B(eq)
Tc(1)	0	0.18276(2)	1/4	1.46(1)
Cl(1)	0	0.40642(6)	1/4	2.20(2)
Cl(2)	0.05476(9)	0.1807(2)	0.4713(2)	2.03(5)
O	-0.0696(3)	0.1673(5)	-0.0276(4)	3.2(2)
N(1)	0	-0.0122(2)	1/4	1.89(8)
N(2)	-0.1133(1)	0.1884(1)	0.2429(1)	1.71(5)
N(4)	-0.0427(4)	0.1768(6)	0.0834(5)	2.0(1)
C(11)	-0.0648(1)	-0.0764(2)	0.1764(2)	2.62(8)
C(12)	-0.0661(2)	-0.2030(2)	0.1749(3)	3.8(1)
C(15)	0	-0.2667(3)	1/4	4.4(2)
C(21)	-0.1675(1)	0.2663(2)	0.1649(2)	2.11(7)
C(22)	-0.2392(1)	0.2819(2)	0.1638(2)	2.75(8)
C(23)	-0.2559(1)	0.2167(2)	0.2468(3)	3.2(1)
C(24)	-0.2014(1)	0.1349(2)	0.3274(2)	2.99(9)
C(25)	-0.1314(1)	0.1224(2)	0.3223(2)	2.31(7)
N(1S)	0.7279(1)	0.0409(2)	0.5269(2)	4.3(1)
C(1S)	0.6748(1)	0.0350(2)	0.5448(2)	2.96(9)
C(2S)	0.6071(1)	0.0261(3)	0.5680(2)	3.7(1)
H(1)	-0.111	-0.033	0.107	2.3
H(2)	-0.118	-0.252	0.123	5.4
H(5)	0	-0.355	1/4	4.7
H(6)	-0.161	0.308	0.098	2.5
H(7)	-0.279	0.337	0.102	3.0
H(8)	-0.307	0.213	0.241	3.1
H(9)	-0.211	0.086	0.382	2.7
H(10)	-0.096	0.075	0.370	2.1
H(16)	0.577	0.099	0.547	3.6
H(17)	0.571	-0.040	0.513	3.6
H(18)	0.622	0.002	0.650	3.6

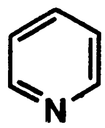
Table II-3. Selected Bond Distances and Angles for *mer*-$[Tc(NO)Cl_2(py)_3]\cdot 2CH_3CN$.

Bond Lengths (Å)		Bond Angles (deg.)	
Tc-Cl1	2.4319(7)	Cl1-Tc-Cl2	90.54(4)
Tc-Cl2	2.367(2)	Cl1-Tc-N1	180.00
Tc-N1	2.120(2)	Cl1-Tc-N2	88.36(4)
Tc-N2	2.138(2)	Cl1-Tc-N2	88.36(4)
Tc-N2	2.138(2)	Cl1-Tc-N4	92.1(2)
Tc-N4	1.781(5)	Cl2-Tc-N1	89.46(4)
O-N4	1.192(5)	Cl2-Tc-N2	88.84(6)
		Cl2-Tc-N2	91.19(6)
		Cl2-Tc-N4	177.2(2)
		N1-Tc-N2	91.64(4)
		N1-Tc-N2	91.64(4)
		N1-Tc-N4	87.9(2)
		N2-Tc-N2	176.72(8)
		N2-Tc-N4	90.3(2)
		N2-Tc-N4	89.8(2)
		Tc-N4-O	176.8(7)

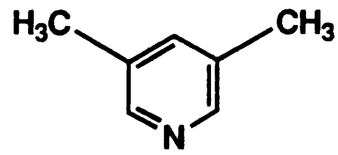
Table II-4. A Comparison of Structural Parameters of *mer*-$[Tc(NO)Cl_2(py)_3]$ and *mer*-$[Tc(NS)Cl_2(pic)_3]$. Bond distances are in Angstroms (Å); angles are in degrees (°).

	$[Tc(NO)Cl_2(py)_3]$	$[Tc(NS)Cl_2(pic)_3]$
Tc^{I}-$N_{nitrosyl}$	1.781(5)	
Tc^{I}-$N_{thionitrosyl}$		1.73(1)
Tc^{I}-$N_{pyridine}$	2.120(2)	2.129(6)
	2.138(2)	2.14(1)
	2.138(2)	2.15(2)
Tc^{I}-Cl_{cis}	2.4319(7)	2.430(2)
Tc^{I}-Cl_{trans}	2.367(2)	2.443(1)
Tc-N-O	176.8(7)	
Tc-N-S		176.0(1)
Reference	this work	10

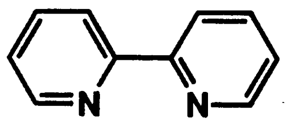
Figure II-1. Structures of the aromatic nitrogen ligands used in this study.



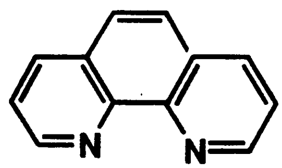
pyridine (py)



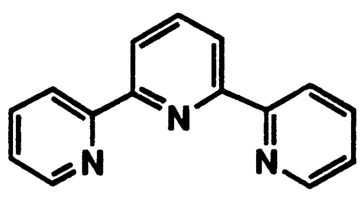
3,5-lutidine (lut)



2,2'-bipyridine (bipy)



1,10-phenanthroline (phen)



2,2':6',2"-terpyridine (terpy)

Figure II-2. Scheme for the reaction of $[Tc(NO)Cl_2(PPh_3)_2(NCCH_3)]$ with pyridine and the conversion between products.

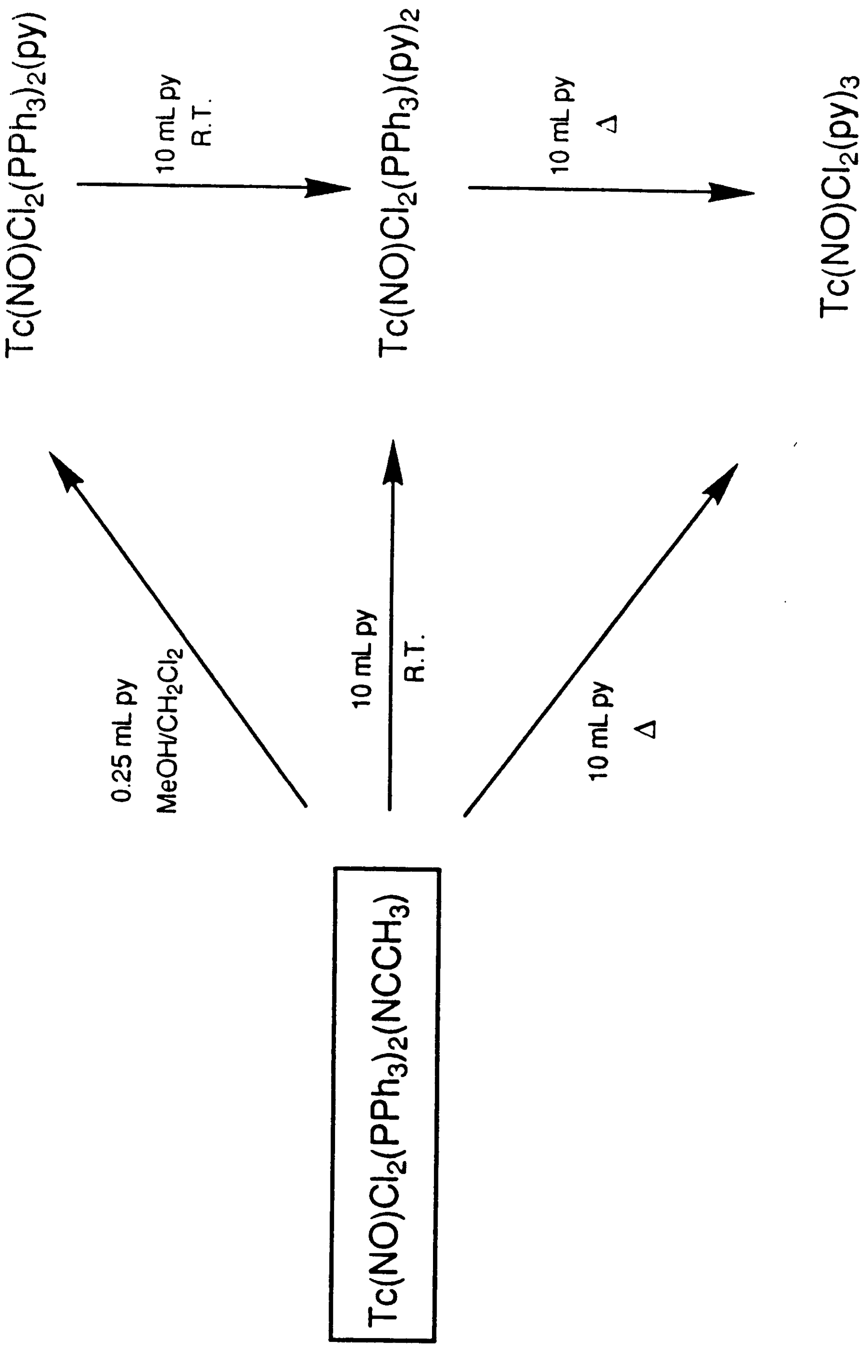

Tc(NO)Cl2(PPh3)2(NCCH3)
0.25 mL py
MeOH/CH2Cl2
10 mL py
R.T.
10 mL py
Δ
Tc(NO)Cl2(PPh3)2(py)
Tc(NO)Cl2(PPh3)(py)2
Tc(NO)Cl2(py)3

Figure II-3. ^{1}H-NMR spectra of $[Tc(NO)Cl_2(PPh_3)(py)_2]$ (A) and $[Tc(NO)Cl_2(PPh_3\text{-}d_{15})(py)_2]$ (B) in CD_2Cl_2. The signals resulting from the α, β, and γ pyridine protons are labelled in Spectrum B.

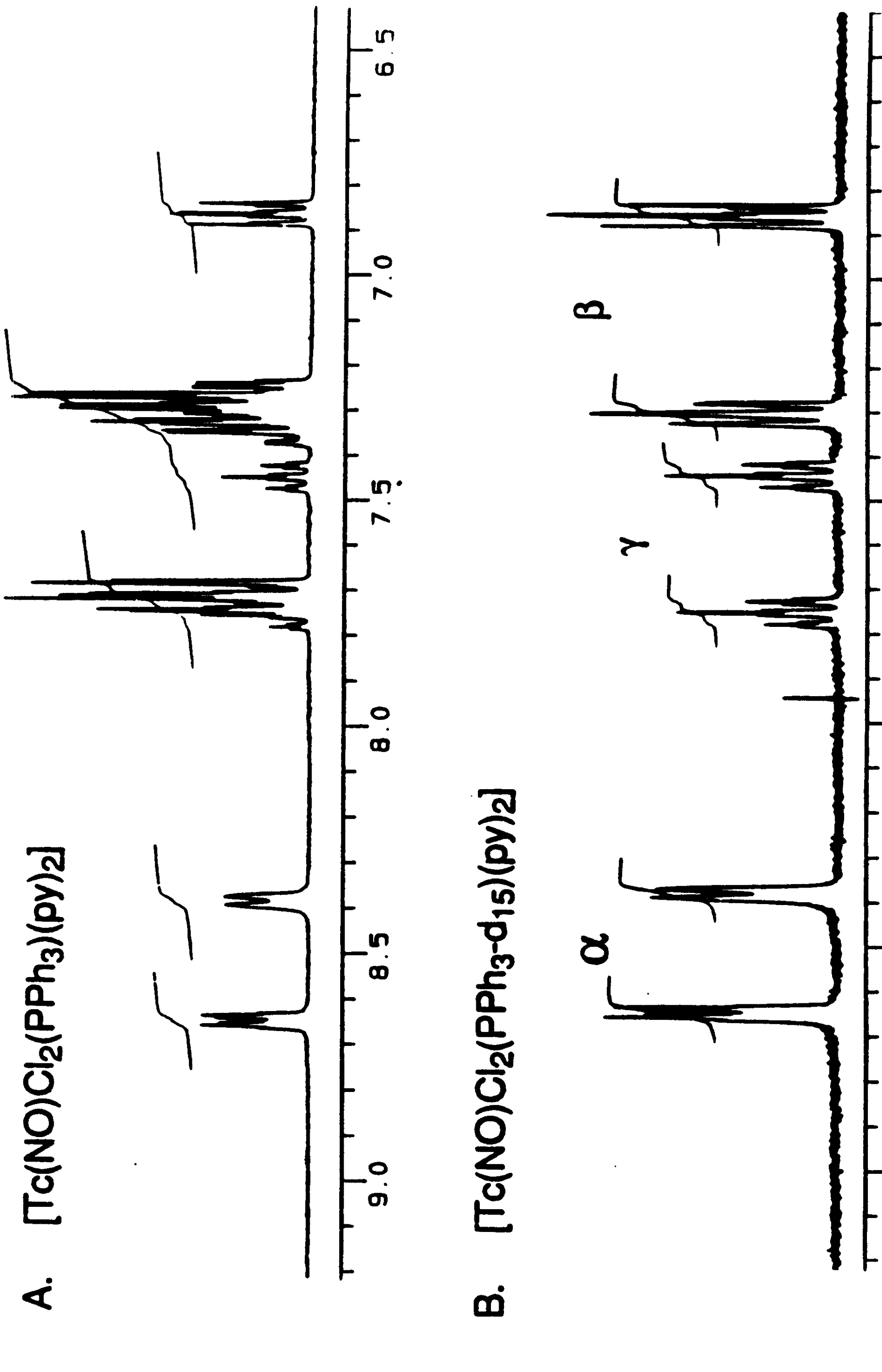
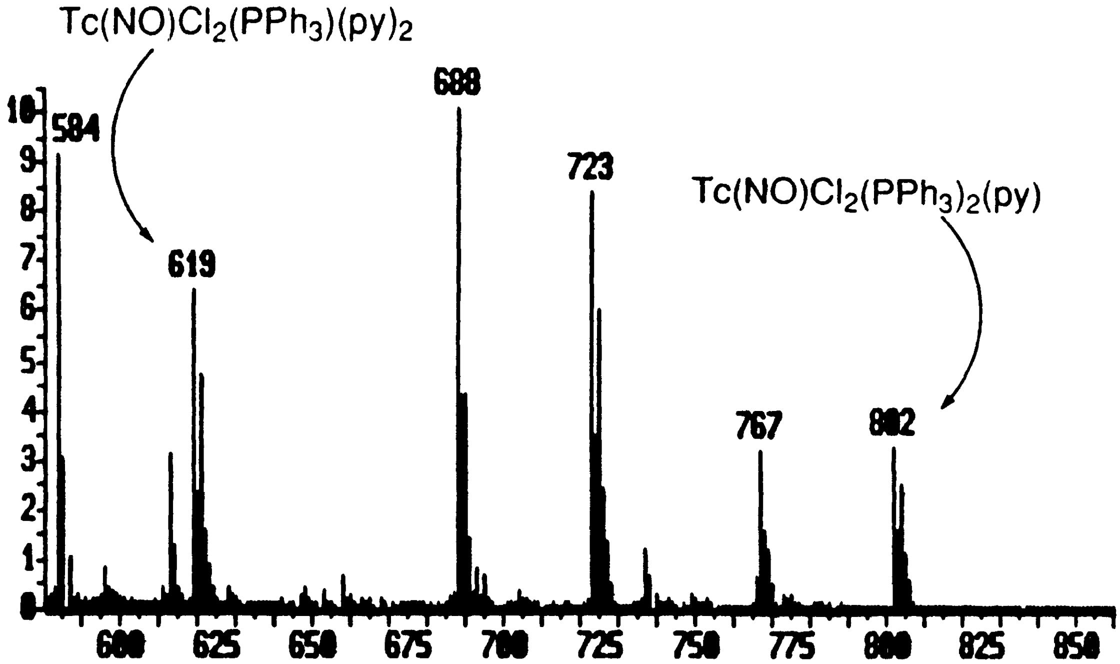
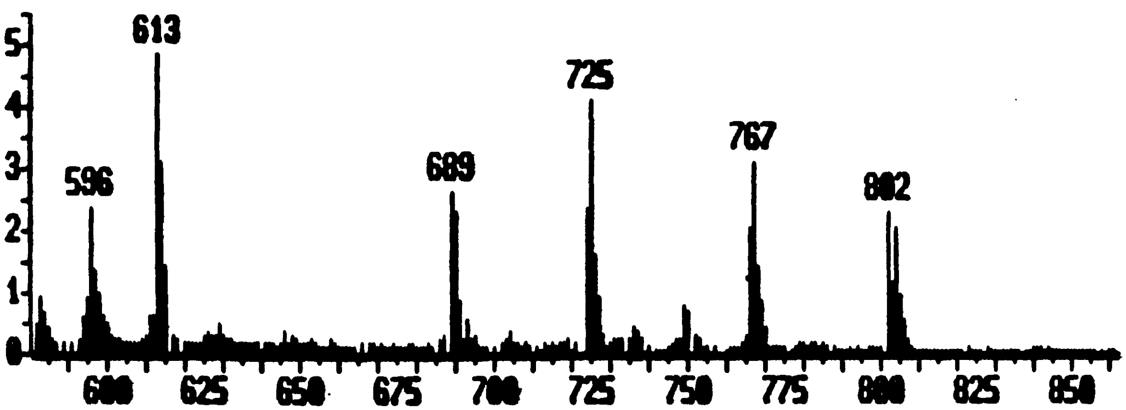

A. [Tc(NO)Cl$_2$(PPh$_3$)(py)$_2$]
B. [Tc(NO)Cl$_2$(PPh$_3$-d$_{15}$)(py)$_2$]
α
γ
β
9.0
8.5
8.0
7.5
7.0
6.5

Figure II-4. Fast atom bombardment mass spectrum (+) of a mixture of $[Tc(NO)Cl_2(PPh_3)_2(py)]$ and $[Tc(NO)Cl_2(PPh_3)(py)_2]$ (A). Mass spectrum of $[Tc(NO)Cl_2(PPh_3)_2(py)]$ after purification (B).


Tc(NO)Cl2(PPh3)(py)2
Tc(NO)Cl2(PPh3)2(py)
584
619
688
723
767
802
600
625
650
675
700
725
750
775
800
825
850

A


596
613
689
725
767
802
600
625
650
675
700
725
750
775
800
825
850

B

Figure II-5. ORTEP[26] representation of the structure of *mer*-$[Tc(NS)Cl_2(pic)_3]$[10] showing 30% probability ellipsoids.

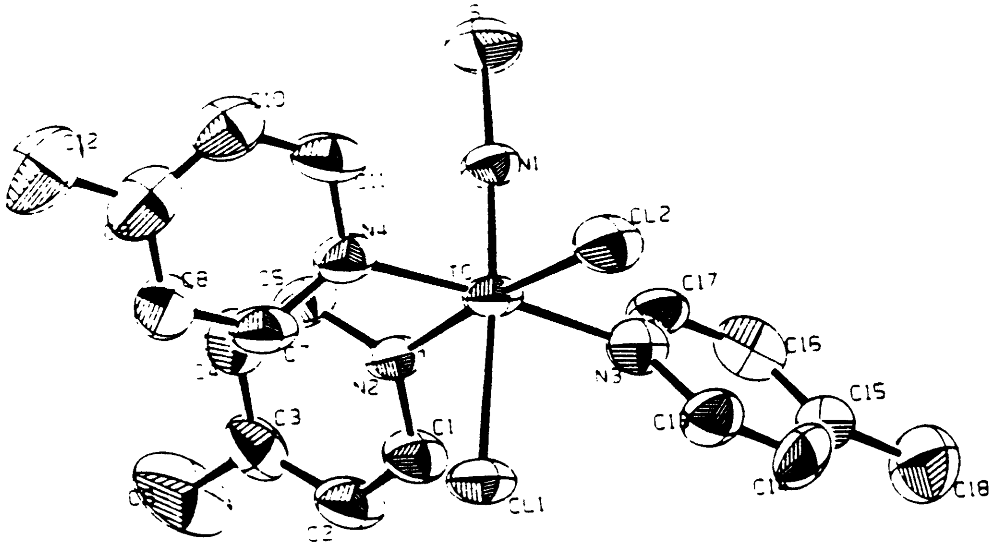

C12
C10
C11
N1
N4
CL2
C8
C5
TC
C17
C16
N2
N3
C15
C3
C1
C18
CL1
C2

Figure II-6. ^1H-NMR spectrum of $[Tc(NO)Cl_2(py)_3]$ in CD_2Cl_2 showing signals resulting from the α, β, and γ pyridine protons.

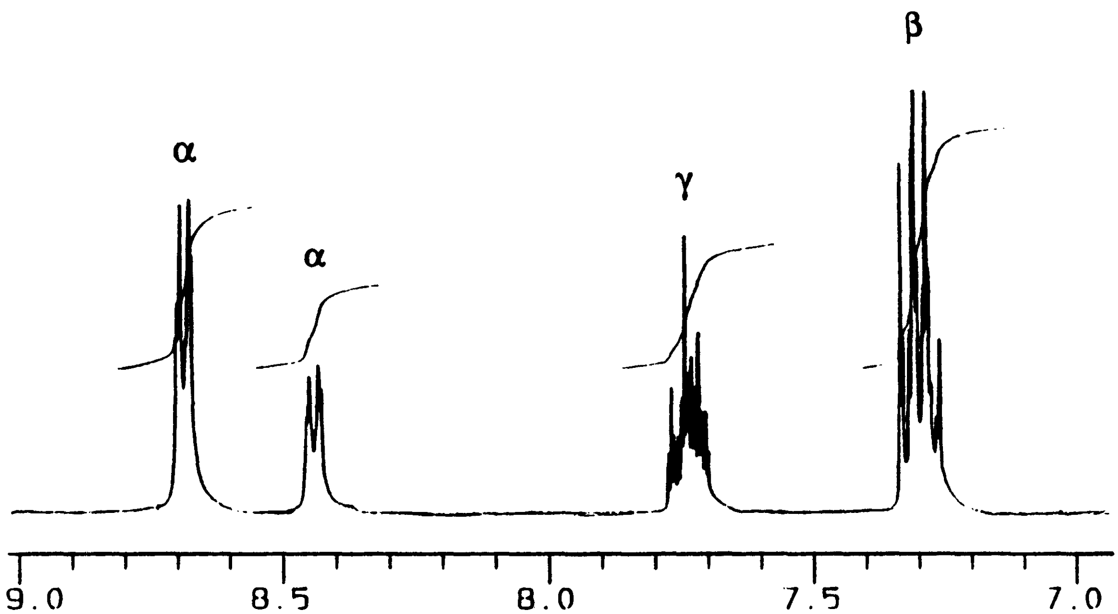

α
α
γ
β
9.0
8.5
8.0
7.5
7.0

Figure II-7. PLUTO[25] diagram of *mer*-$[Tc(NO)Cl_2(py)_3]\cdot 2CH_3CN$.

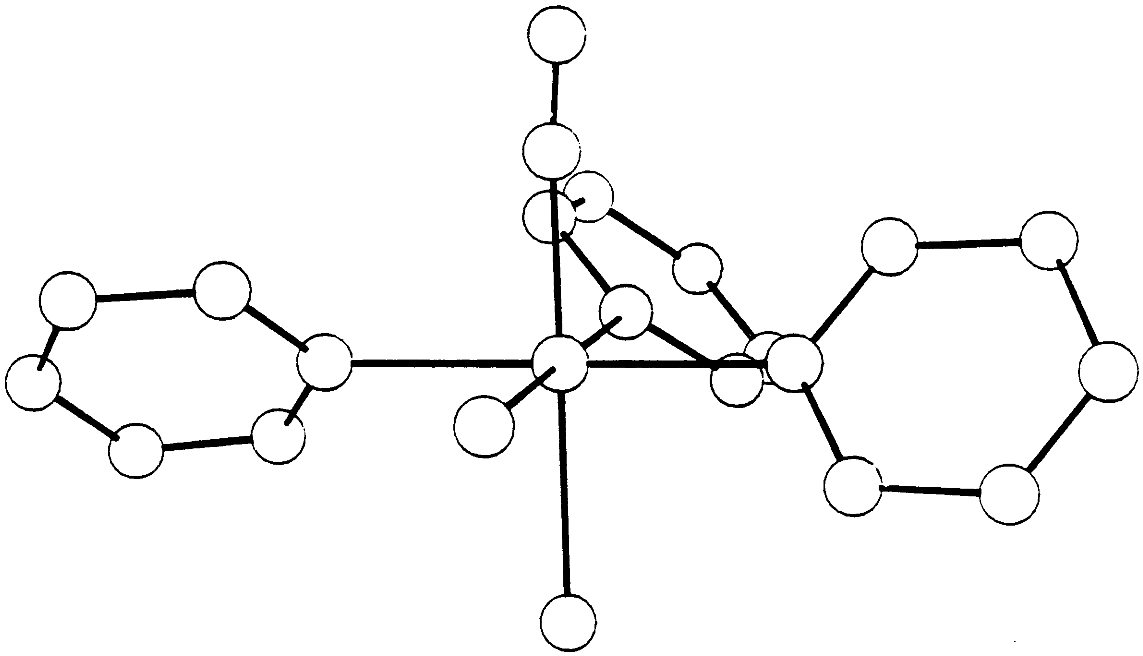
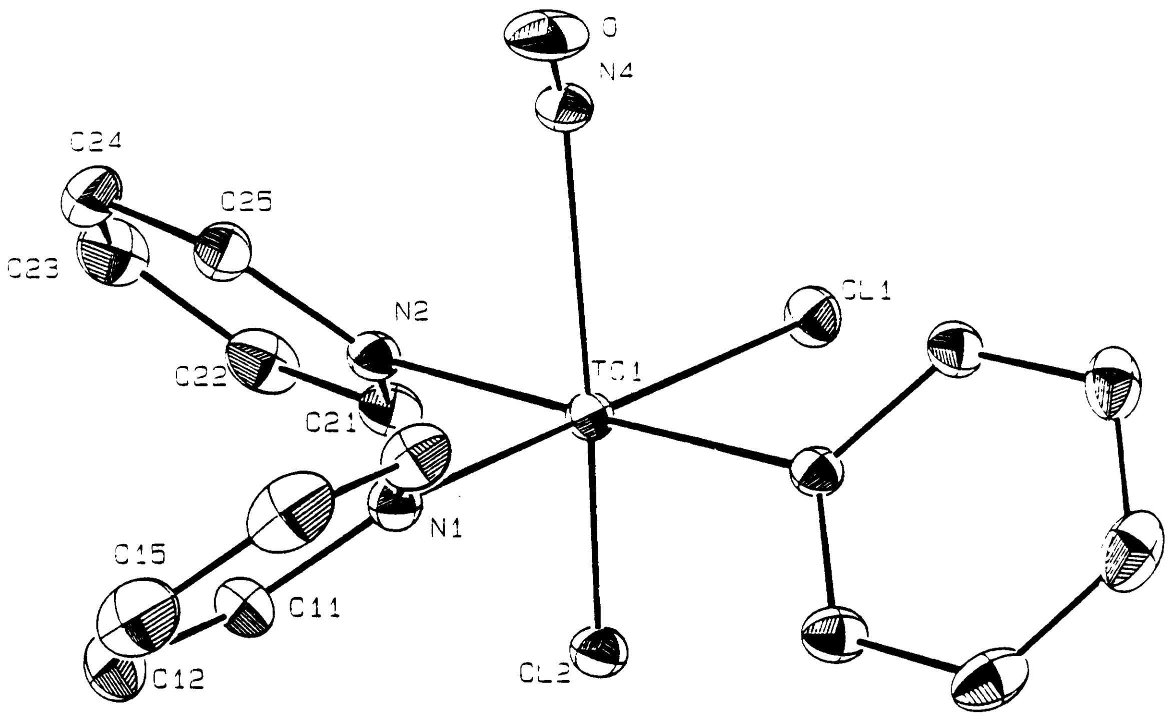


Figure II-8. ORTEP[26] representation of *mer*-$[Tc(NO)Cl_2(py)_3]\cdot 2CH_3CN$ **[3]** showing the atom labelling scheme and 35% probability ellipsoids.



O
N4
C24
C25
C23
N2
CL1
TC1
C22
C21
N1
C15
C11
CL2
C12

Figure II-9. Scheme for the reaction of $[Tc(NO)Cl_2(PPh_3)_2(NCCH_3)]$ with multidentate aromatic amines.

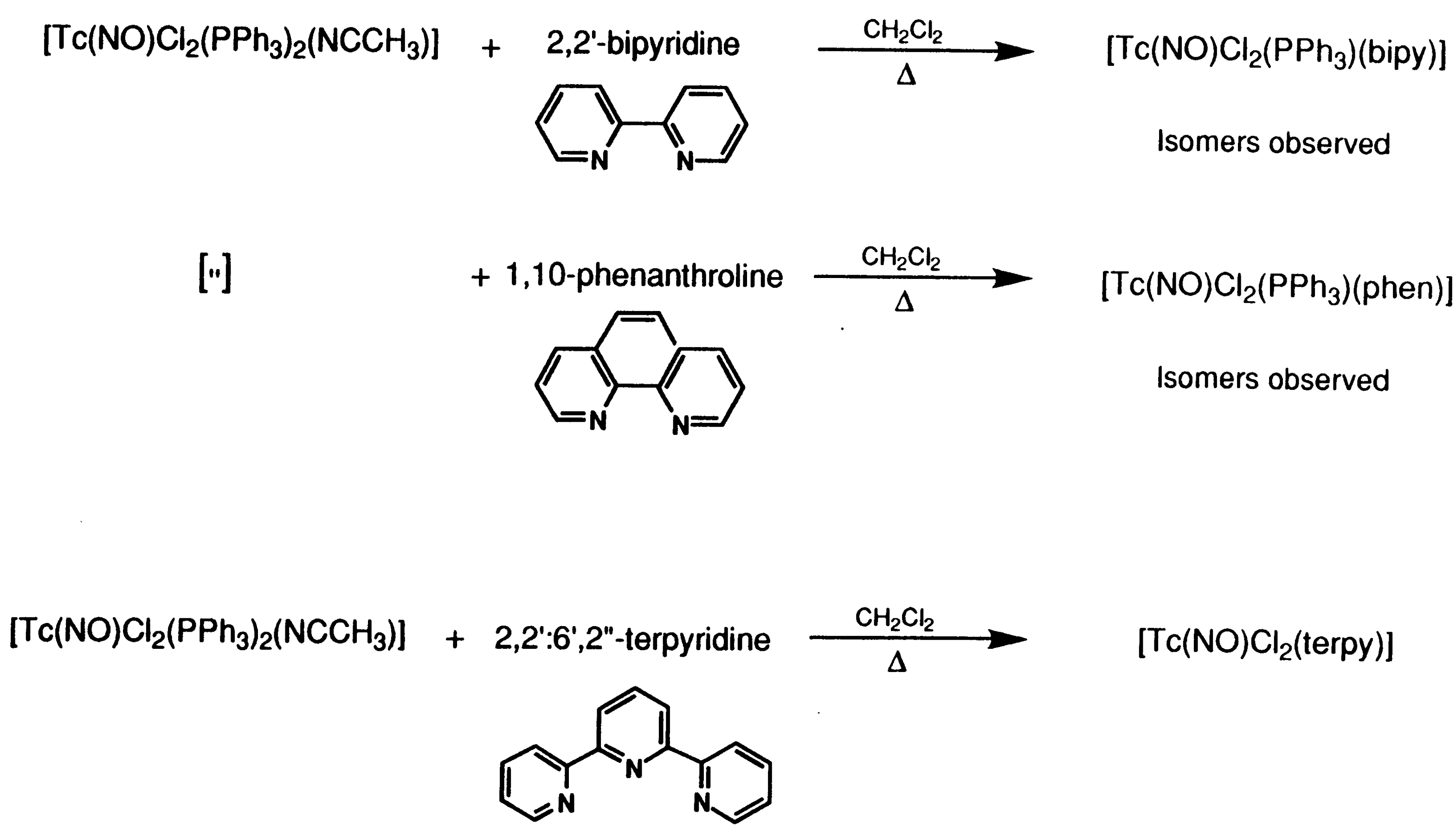
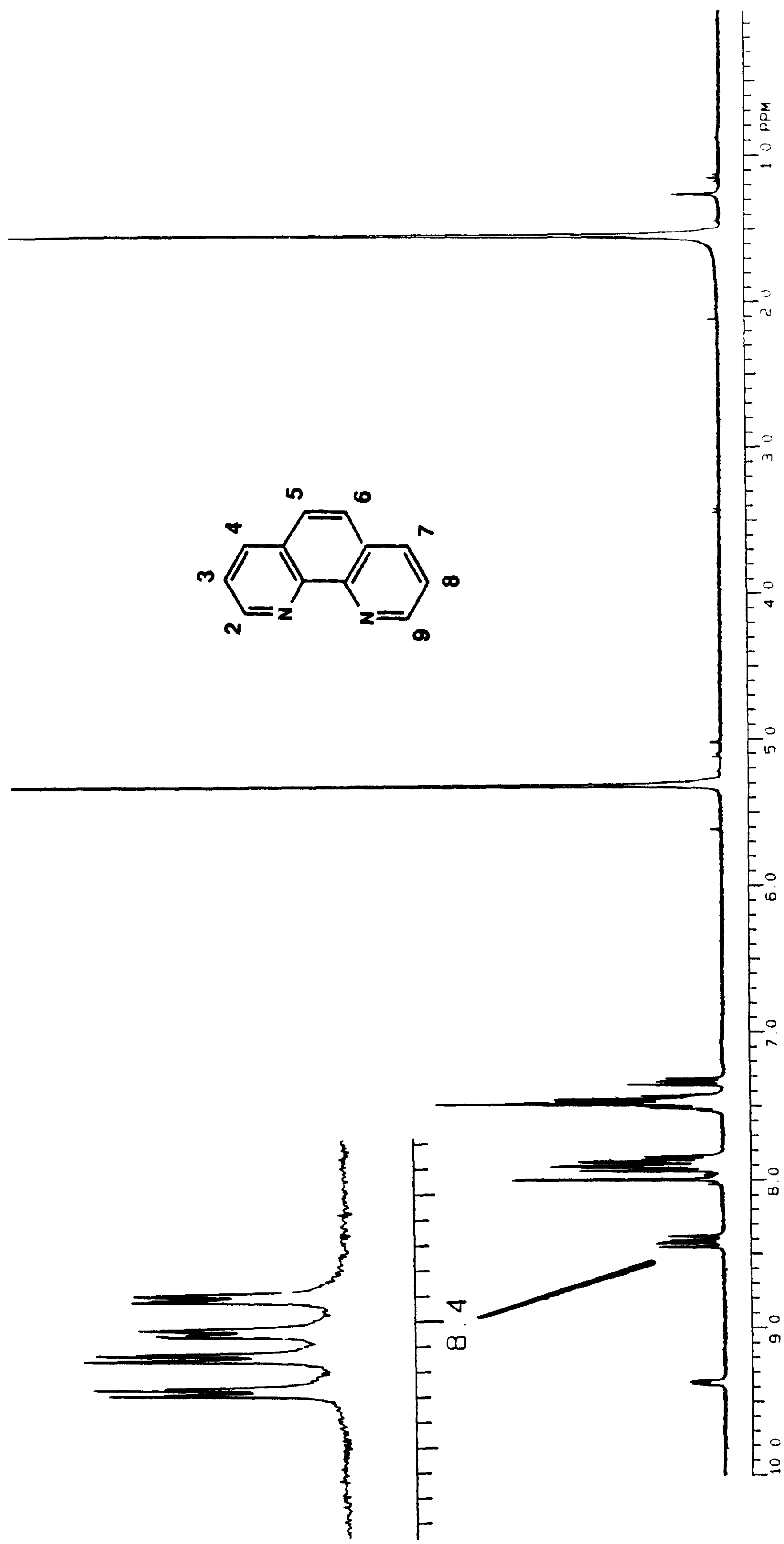

[Tc(NO)Cl$_2$(PPh$_3$)$_2$(NCCH$_3$)] + 2,2'-bipyridine
CH$_2$Cl$_2$
Δ
[Tc(NO)Cl$_2$(PPh$_3$)(bipy)]
Isomers observed
N
N
["]
+ 1,10-phenanthroline
CH$_2$Cl$_2$
Δ
[Tc(NO)Cl$_2$(PPh$_3$)(phen)]
Isomers observed
N
N
[Tc(NO)Cl$_2$(PPh$_3$)$_2$(NCCH$_3$)] + 2,2':6',2"-terpyridine
CH$_2$Cl$_2$
Δ
[Tc(NO)Cl$_2$(terpy)]
N
N
N

Figure II-10. ^1H-NMR spectrum of $[Tc(NO)Cl_2(PPh_3)(phen)]$ in CD_2Cl_2.



1.0 PPM
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
8.4

CHAPTER III

Ligand Substitution Reactions of $[Tc(NO)Cl_2(PPh_3)_2(NCCH_3)]$ with π-Acceptor Ligands

Introduction

While the π-accepting ligands carbon monoxide and *tert*-butylisonitrile are known to stabilize metals in low oxidation states,[1] little is known of their reaction chemistry with technetium nitrosyl complexes. The technetium(I) complexes $[Tc(NO)(CNtBu)_5](PF_6)_2$ and $[Tc(NO)Br_2(CNtBu)_3]$ are the only known nitrosyl-technetium compounds with isonitrile ligation.[2] This is surprising considering the ubiquitous nature of the ligand in inorganic coordination chemistry[3] and the success of such technetium complexes in nuclear medicine.[4,5] No carbonyl-nitrosyltechnetium complexes have been characterized to date. In comparison, a wealth of chemistry is known about these complexes of rhenium, manganese, iron, iridium, and other transition metals.

The ease of ligand exchange in $[Tc(NO)Cl_2(PPh_3)_2(NCCH_3)]$ **[2]** allows the preparation of several new nitrosyltechnetium(I) complexes using carbon monoxide and *tert*-butylisonitrile. The reactions follow the predicted course of sequential neutral ligand substitution, as established in Chapter 2 for the reactions of **[2]** with aromatic amines. These reactions show the versatility of $[Tc(NO)Cl_2(PPh_3)_2(NCCH_3)]$ as a starting material in the synthesis of low valent nitrosyltechnetium complexes.

Experimental Section

Caution: Technetium-99 is a weak β^- emitter (E=292 keV, $t_{1/2}$= 2.12 x 10^5 years). All manipulations of solutions and solids were performed in laboratories approved for the use of low-level radioactivity, following precautions detailed elsewhere.[6]

Ammonium pertechnetate was obtained as a gift from Du Pont Merck Pharmaceutical Company. The starting material, $[Tc(NO)Cl_2(PPh_3)_2(NCCH_3)]$ **[2]**, was synthesized as described in Chapter 1, and $Me_4N[Tc(NO)Br_4]$ was prepared according to literature methods.[7,8] Carbon monoxide (CO) was purchased from Matheson Gas Products, and *tert*-butylisonitrile (CNtBu) was obtained from Aldrich Chemical Company. Solvents were of at least reagent grade; solvents and reagents were used as received unless otherwise indicated. Column chromatography was performed with ICN Biomedicals Alumina N, Activity I.

Fast atom bombardment mass spectra (FABMS) were recorded with a MAT 731 mass spectrometer equipped with an Ion Tech B11N FAB gun that produced a beam of 6-8 keV Xenon neutrals. The samples were dissolved in a *p*-nitrobenzyl alcohol matrix. Peaks resulting from the most abundant isotopes of chlorine and bromine are referenced in the mass spectra: ^{35}Cl, ^{79}Br, or $^{79}Br^{81}Br$. Routine infrared spectra were recorded on a Mattson Cygnus 100 FT spectrophotometer or on a Perkin-Elmer 1600 Series FTIR. ^1H and ^{99}Tc NMR spectra were recorded at room temperature using a Varian XL-300 MHz spectrometer. The primary reference for ^{99}Tc-NMR, $[NH_4][^{99}TcO_4]$ in D_2O, resonates at 67.516 MHz and is designated as 0 ppm. A 34-µs pulse width (90° tip) and 0.15-s acquisition time were used. No additional relaxation delay was employed. For differences greater than the maximum spectral width (10^5 Hz, 1480 ppm) obtainable, chemical shifts could be calculated based on the spectrometer frequency, transmitter offset, transmitter base offset, and relative shift within the spectral window. We estimate that the error associated with these values is ±2 ppm. The presence of spectral folding or other artifacts was ruled out by changing the transmitter offset by a known frequency and verifying that the resonance moved within the spectral window by the appropriate amount and in the expected direction.[9] Magnetic susceptibility studies were performed on a Cahn Model 7500 electrobalance at 25 °C. Elemental analyses were performed by Atlantic Microlab Inc., Norcross, GA.

Preparation of [carbonyldichloronitrosylbis(triphenylphosphine) technetium(I)], [$Tc(NO)Cl_2(PPh_3)_2(CO)$] [15].

A sample of solid [$Tc(NO)Cl_2(PPh_3)_2(NCCH_3)$] **[2]** (91.8 mg, 0.12 mmol) was added to previously degassed chloroform (50 mL) saturated with carbon monoxide, and the suspension was stirred at room temperature until the solid dissolved. Carbon monoxide was bubbled through the reaction mixture for three hours, until a light green-yellow solution had been achieved. The solution was filtered and concentrated to 3 - 4 mL under reduced pressure. Excess pentane (45 mL) was added to initiate the precipitation of a pale green-yellow solid. The precipitate was collected on a fritted glass funnel, rinsed with pentane (10 mL) and diethyl ether (10 mL), and dried in vacuo. Yield 75.5 mg (83.7%) of [$Tc(NO)Cl_2(PPh_3)_2(CO)$]$\cdot H_2O$. The product can be recrystallized from a layered mixture of dichloromethane, methanol, and diethyl ether (1:1:15) to yield yellow X-ray quality crystals.

Anal. Calcd for $C_{37}H_{32}Cl_2NO_3P_2Tc$: C, 57.66; H, 4.16; Cl, 9.22; N, 1.82.

Found: C, 57.79; H, 4.02; Cl, 9.33; N, 1.93.

FABMS(+) (*m/z*): 770 $[Tc(NO)Cl_2(PPh_3)_2(CO)\cdot H_2O + H]^+$,

723 $[Tc(NO)Cl_2(PPh_3)_2]^+$, 716 $[Tc(NO)Cl(PPh_3)_2(CO)]^+$,

688 $[Tc(NO)Cl(PPh_3)_2]^+$.

IR (KBr) (cm^{-1}): ν (NO) 1747 (vs), 1757 (sh), 1776 (s).

ν (CO) 2016 (vs), 2020 (sh), 2039 (s).

($CHCl_3$): ν (NO) 1760 (vs, br).

ν (CO) 2031 (vs).

^1H-NMR (CD_2Cl_2): δ=7.82 (m, 2H), 7.44 (m, 3H).

^{99}Tc-NMR (CD_2Cl_2): δ= - 618 ppm, linewidth 2480 Hz (δ TcO_4^- is 0 ppm).

An increase in the solution temperature had no effect on the product formed in this reaction. The reaction of **[2]** (60.6 mg, 0.079 mmol) with carbon monoxide in a refluxing benzene/dichloromethane (4:1) solution also produced compound **[15]** in good yields (50.1 mg, 84.4%).

Reaction of [15] with Pyridine: Preparation of [dichloronitrosyl tripyridinetechnetium(I)], $[Tc(NO)Cl_2(py)_3]$ [3].

A sample of **[15]** (46.8 mg, 0.062 mmol) was dissolved in pyridine (5 mL) and refluxed for twenty-four hours. After cooling to room temperature, the resulting cherry-red solution was flooded with excess diethyl ether (100 mL). Upon refrigeration , the cloudy red solution yielded a cherry-red microcrystalline solid. The product was collected on a fritted glass funnel, rinsed with pentane (10 mL), and dried in vacuo. Yield 18.8 mg (69.1%).

The isolated material was spectroscopically identical to yields obtained in the preparations of [$Tc(NO)Cl_2(py)_3$] **[3]** which are described in Chapters 1 and 2.

Preparation of [acetonitriledibromonitrosylbis(triphenylphosphine) technetium(I)], [$Tc(NO)Br_2(PPh_3)_2(NCCH_3)$] [16].

This compound was prepared analogously to **[2]** from triphenylphosphine (275.1 mg, 1.05 mmol) and $Me_4N[Tc(NO)Br_4]$ (77.9 mg, 0.15 mmol) in acetonitrile (15 mL). Yield 96.3 mg (75.4%) of the orange-red solid [$Tc(NO)Br_2(PPh_3)_2(NCCH_3)$]$\cdot H_2O$. The complex is soluble in dichloromethane and chloroform but slowly decomposes over time.

Anal. Calcd for $C_{38}H_{35}Br_2N_2O_2P_2Tc$: C, 52.41; H, 4.02; Br, 18.16; N, 3.22.

Found: C, 52.25; H, 3.90; Br, 18.43; N, 3.19.

FABMS(+) (*m/z*): 854 [$Tc(NO)Br_2(PPh_3)_2(NCCH_3)$]$^+$, 813 [$Tc(NO)Br_2(PPh_3)_2$]$^+$, 732 [$Tc(NO)Br(PPh_3)_2$]$^+$.

IR (KBr) (cm^{-1}): ν (NO) 1719 (vs, br)

^1H-NMR (CD_2Cl_2): δ=7.92 (m, 12H), 7.38 (m, 19H), 1.97 (s, 0.53H), 1.37 (s, 2.47H).

^{99}Tc-NMR (CD_2Cl_2): δ= 582 ppm, linewidth 5460 Hz (δ TcO_4^- is 0 ppm).

Magnetic Susceptibility: diamagnetic in solid state

Preparation of [dibromocarbonylnitrosylbis(triphenylphosphine) technetium(I)], [$Tc(NO)Br_2(PPh_3)_2(CO)$] [17].

This complex was synthesized analogously to **[15]**, using [$Tc(NO)Br_2(PPh_3)_2(NCCH_3)$] **[16]** (37.8 mg, 0.044 mmol) as the starting material in the reaction with carbon monoxide. Yield 31.8 mg (86.1%) of a pale green-yellow solid.

Anal. Calcd for $C_{37}H_{30}Br_2NO_2P_2Tc$: C, 52.92; H, 3.58; Br, 18.83; N, 1.67.

Found: C, 51.11[10]; H, 3.39; Br, 19.03; N, 1.66.

FABMS(+) (*m/z*): 813 [$Tc(NO)Br_2(PPh_3)_2$]$^+$, 760 [$Tc(NO)Br(PPh_3)_2(CO)$]$^+$, 732 [$Tc(NO)Br(PPh_3)_2$]$^+$.

IR (KBr) (cm^{-1}): ν (NO) 1744 (vs), 1757 (s).

ν (CO) 2010 (s), 2023 (vs).

($CHCl_3$): ν (NO) 1762 (vs, br), 1752 (sh).

ν (CO) 2031 (vs).

^{1}H-NMR (CD_2Cl_2): δ=7.84 (m, 2H), 7.43 (m, 3H).

^{99}Tc-NMR (CD_2Cl_2): δ= - 673 ppm, linewidth 2850 Hz (δ TcO_4^- is 0 ppm).

Preparation of [(*tert*-butylisonitrile)dichloronitrosylbis(triphenylphosphine) technetium(I)], [$Tc(NO)Cl_2(PPh_3)_2(CNtBu)$] [18].

A small amount of *tert*-butylisonitrile (0.15 mL, 1.32 mmol) was added to a solution of complex **[2]** (56.7 mg, 0.074 mmol) in dichloromethane (15 mL). After stirring at room temperature for one hour, the dark orange solution was evaporated to dryness under reduced pressure. The orange residue was dissolved in 1.5 mL dichloromethane and chromatographed on an alumina column conditioned and washed with pentane (100 mL). A yellow band was eluted with diethyl ether (400 mL) and filtered. The yellow fraction was dried completely using rotary evaporation to yield a lemon yellow residue, which was then dissolved in benzene (6 mL). Addition of excess pentane (25 mL) caused the product to precipitate as a dull yellow solid. The product was collected on a fritted glass funnel, rinsed with pentane (10 mL), and dried in vacuo. Yield 40.9 mg (68.5%) of $[Tc(NO)Cl_2(PPh_3)_2(CNtBu)]\cdot 0.5\ H_2O$. The product can be recrystallized from layered benzene/methanol/hexane (2:1:10) to yield brass colored (orange-yellow) crystals. Slow decomposition in dichloromethane causes a brown solution to be formed after several days.

Anal. Calcd for $C_{41}H_{40}Cl_2N_2O_{1.5}P_2Tc$: C, 60.29; H, 4.90; Cl, 8.70; N, 3.43.

Found: C, 60.30; H, 4.80; Cl, 8.79; N, 3.41.

FABMS(+) (*m/z*): 806 $[Tc(NO)Cl_2(PPh_3)_2(CNtBu)]^+$,

771 $[Tc(NO)Cl(PPh_3)_2(CNtBu)]^+$, 723 $[Tc(NO)Cl_2(PPh_3)_2]^+$,

688 $[Tc(NO)Cl(PPh_3)_2]^+$, 544 $[Tc(NO)Cl_2(PPh_3)(CNtBu)]^+$.

509 $[Tc(NO)Cl(PPh_3)(CNtBu)]^+$, 461 $[Tc(NO)Cl_2(PPh_3)]^+$,

453 $[Tc(NO)Cl(PPh_3)CN + H]^+$.

IR (KBr) (cm^{-1}): ν (NO) 1703 (s), 1737 (vs).

ν (CN) 2171 (vs).

($CHCl_3$): ν (NO) 1748 (vs, br).

ν (CN) 2247 (w), 2157 (vs).

^1H-NMR (CD_2Cl_2): δ=7.85 (m, 12H), 7.40 (m, 20H), 0.90 (s, 7.5H), 0.82 (s, 1.5H).

(4:1 C_6D_6/CD_2Cl_2): δ=8.04 (m, 12H), 7.06 (m, 18H), 0.60 (s, 6.4H), 0.56 (s, 2.6H).

^{99}Tc-NMR (3:1 C_6D_6/CD_2Cl_2): δ= - 329 ppm, linewidth 4090 Hz (δ TcO_4^- is 0 ppm).

Preparation of [bis(*tert*-butylisonitrile)dichloronitrosyl(triphenylphosphine) technetium(I)], [$Tc(NO)Cl_2(PPh_3)(CNtBu)_2$] [19].

A mixture of compound **[2]** (58.1 mg, 0.076 mmol) and excess *tert*-butylisonitrile (2 mL, 17.7 mmol) in dichloromethane (10 mL) was refluxed for twenty-four hours to form a yellow solution. The sample was concentrated to 1.5 mL under reduced pressure and chromatographed on an alumina column conditioned and washed with pentane (100 mL). The column was washed with diethyl ether (100 mL) to remove traces of complex **[18]**. A yellow fraction was then eluted with acetonitrile (75 mL) and filtered. After the solvent was removed using rotary evaporation, the yellow residue was dissolved in dichloromethane (2 mL). Excess pentane (25 mL) was added to cause the product to precipitate as a pale yellow solid. The solid was collected on a fritted glass funnel, rinsed with pentane (5 mL), and dried in vacuo. Yield 22.9 mg (48.0%) of the pale yellow solid [$Tc(NO)Cl_2(PPh_3)(CNtBu)_2$]·0.33 H_2O.

Anal. Calcd for $C_{28}H_{33.67}Cl_2N_3O_{1.33}PTc$: C, 53.00; H, 5.31; Cl, 11.20; N, 6.62.

Found: C, 53.01; H, 5.29; Cl, 10.59; N, 6.94.

FABMS(+) (*m/z*): 627 [$Tc(NO)Cl_2(PPh_3)(CNtBu)_2$]$^+$,

592 [$Tc(NO)Cl(PPh_3)(CNtBu)_2$]$^+$, 544 [$Tc(NO)Cl_2(PPh_3)(CNtBu)$]$^+$,

509 [$Tc(NO)Cl(PPh_3)(CNtBu)$]$^+$, 461 [$Tc(NO)Cl_2(PPh_3)$]$^+$,

453 [$Tc(NO)Cl(PPh_3)CN$ + H]$^+$.

IR (KBr) (cm^{-1}): ν (NO) 1736 (vs).

ν (CN) 2200 (s), 2168 (s).

^{1}H-NMR (CD_2Cl_2): δ=7.77 (m, 7H), 7.41 (m, 10H), 1.59 (s, 9H), 1.29 (s, 9H).

^{99}Tc-NMR (CD_2Cl_2): δ= - 380 ppm, linewidth 4700 Hz (δ TcO_4^- is 0 ppm).

Preparation of [tris(*tert*-butylisonitrile)dichloronitrosyltechnetium(I)], $[Tc(NO)Cl_2(CNtBu)_3]$ [20].

Excess *tert*-butylisonitrile (2.5 mL, 22.1 mmol) was added to a suspension of complex **[2]** (83.5 mg, 0.109 mmol) in benzene (15 mL), and the mixture was refluxed for thirty-six hours to yield a yellow solution. The sample volume was reduced to 1.5 mL by rotary evaporation, and the solution was chromatographed on an alumina column conditioned and washed with diethyl ether (100 mL) to elute traces of **[19]** as a pale yellow band. A bright yellow band was eluted with a 50% (v/v) solution of acetonitrile/diethyl ether. The bright yellow fraction was filtered and concentrated to 0.5 mL under reduced pressure. The resulting yellow oil was taken up in a minimum amount of dichloromethane (1 - 2 mL). Excess pentane (25 mL) was added to form a cloudy yellow solution, which precipitated a fine yellow solid upon standing at room temperature for one hour. The product was collected on a fritted glass funnel, washed with pentane (5 mL), and dried in vacuo. Yield 33.3 mg (68.0%).

Anal. Calcd for $C_{15}H_{27}Cl_2N_4OTc$: C, 40.09; H, 6.01; Cl, 15.81; N, 12.47.

Found: C, 40.10; H, 6.16; Cl, 15.94; N, 12.37.

FABMS(+) (*m/z*): 448 $[Tc(NO)Cl_2(CNtBu)_3]^+$, 413 $[Tc(NO)Cl(CNtBu)_3]^+$, 392 $[Tc(NO)Cl_2(CNtBu)_2CN + H]^+$, 367 $[Tc(NO)Cl_2(CNtBu)_2 + H]^+$, 357 $[Tc(NO)Cl(CNtBu)_2CN + H]^+$, 336 $[TcCl_2(CNtBu)_2 + H]^+$.

IR (KBr) (cm^{-1}): ν (NO) 1751 (vs), 1725 (vs).

ν (CN) 2214 (m), 2176 (vs).

($CHCl_3$): ν (NO) 1760 (vs, br).

ν (CN) 2214 (m), 2188 (vs), 2173 (sh).

^{1}H-NMR (CD_2Cl_2): δ=1.58 (s, 2H), 1.56 (s, 1H).

^{99}Tc-NMR (CD_2Cl_2): δ= - 498 ppm, linewidth 5700 Hz (δ TcO_4^- is 0 ppm).

Preparation of [dibromotris(*tert*-butylisonitrile)nitrosyltechnetium(I)], [Tc(NO)Br_2(CNtBu)$_3$] [21].

This complex was prepared analogously to **[20]**, substituting [Tc(NO)Br_2(PPh_3)$_2$($NCCH_3$)] **[16]** (50.1 mg, 0.059 mmol) for **[2]**. Yield 20.9 mg (65.8 %) of a yellow solid.

FABMS(+) (*m*/*z*): 537 [Tc(NO)Br_2(CNtBu)$_3$ - H]$^+$, 457 [Tc(NO)Br(CNtBu)$_3$]$^+$, 401 [Tc(NO)Br(CNtBu)$_2$CN + H]$^+$, 373 [Tc(NO)Br(CNtBu)$_2$ - H]$^+$, 344 [TcBr(CNtBu)$_2$]$^+$, 317 [Tc(NO)Br(CNtBu)CN]$^+$.

IR (KBr) (cm^{-1}): ν (NO) 1755 (sh), 1748 (vs), 1734 (vs), 1730 (sh).

ν (CN) 2214 (m), 2182 (vs).

(CH_2Cl_2): ν (NO) 1760 (vs, br).

ν (CN) 2214 (w), 2185 (vs).

^{1}H-NMR (CD_2Cl_2): δ=1.58 (s, 2H), 1.56 (s, 1H).

^{99}Tc-NMR (CD_2Cl_2): δ= - 596 ppm, linewidth 6950 Hz (δ TcO_4^- is 0 ppm).

Results and Discussion

[Tc(NO)X_2(PPh_3)$_2$(CO)] (X is Cl or Br)

The reaction of [Tc(NO)Cl_2(PPh_3)$_2$($NCCH_3$)] **[2]** with carbon monoxide gas in chloroform gives the yellow product [Tc(NO)Cl_2(PPh_3)$_2$(CO)] **[15]** in good yield (**Figure III-1**). The carbon monoxide cleanly replaces the labile acetonitrile molecule of **[2]** under mild conditions. Displacement of the triphenylphosphine ligands is not observed, even when the reaction is performed under refluxing conditions. This type of substitution selectivity has been exhibited in the reactions of similar mixed ligand complexes, [TcCl_3(PPh_3)$_2$($NCCH_3$)],[12] [Tc(SAr)$_3$($NCCH_3$)$_2$][13,14] (SAr is 2,3,5,6-tetramethylbenzenethiolate or 2,4,6-triisopropylbenzenethiolate), [HTc(N_2)(dppe)$_2$][15] [dppe is 1,2-bis(diphenylphosphino)ethane], and [Re(NO)Cl_2(PPh_3)$_2$(OCH_3)],[16] with carbon monoxide; in these reactions, the labile CH_3CN, N_2, or methoxide ligand is replaced by CO, forming the complexes [TcCl_3(PPh_3)$_2$(CO)], [Tc(SAr)$_3$(CO)$_2$], [HTc(CO)(dppe)$_2$], or [Re(NO)Cl_2(PPh_3)$_2$(CO)], respectively.

The characterization of [Tc(NO)Cl_2(PPh_3)$_2$(CO)] **[15]** is straightforward based on comparisons with the rhenium analog.[16,17] The fast atom bombardment mass spectrum of **[15]** displays a molecular ion peak at 770 *m/z*, corresponding to [Tc(NO)Cl_2(PPh_3)$_2$(CO)·H_2O + H]$^+$; fragmentation peaks resulting from the loss of CO (723 *m/z*), Cl (716 *m/z*), and both CO and Cl (688 *m/z*) are also observed. The IR spectrum of **[15]**, taken in chloroform, shows a very strong carbonyl stretching vibration at 2031 cm^{-1} and a broader nitrosyl stretch at 1760 cm^{-1}. Although not expected based on symmetry considerations, multiple NO and CO bands appear in the IR spectrum of **[15]** if it is obtained in KBr; this splitting may occur due to solid state effects in the KBr pellet.[18] Equivalent *trans*-triphenylphosphine ligands can be seen in the ^{1}H-NMR spectrum of $[Tc(NO)Cl_2(PPh_3)_2(CO)]$, and the ^{99}Tc-NMR spectrum of **[15]** yields a ^{99}Tc signal at -618 ppm relative to $[NH_4][^{99}TcO_4]$.

The preparation and characterization of the bromine derivative $[Tc(NO)Br_2(PPh_3)_2(CO)]$ **[17]** is directly analogous with the data obtained from complex **[15]**; the fast atom bombardment mass spectrum of **[17]** displays the isotopic pattern expected for a complex containing two atoms of bromine (**Figure III-2**). The only difference arises in the ^{99}Tc-NMR signal of the bromine analog **[17]**, which is located at -673 ppm and is shifted 55 ppm upfield from the -618 ppm resonance of complex **[15]**; the shift to more negative ppm values upon substitution of Br for Cl occurs due to the greater shielding of the technetium nucleus afforded by the bromine atom.

While spectroscopic data confirm that the bulky phosphine ligands occupy the expected positions *trans* to one another, geometric information about the nitrosyl and carbonyl moieties is not directly available from the characterization techniques employed while studying $[Tc(NO)Cl_2(PPh_3)_2(CO)]$. Since they are both strong π-acid ligands, the NO and CO groups are expected to bind to the technetium in a *cis* configuration (proposed structure, **Figure III-3**). A single crystal X-ray structure determination[19] of $[Tc(NO)Cl_2(PPh_3)_2(CO)]$ could not confirm this *cis* ligand orientation due to crystallographic disorder; the NO, CO, and Cl groups possess a similar number of electrons and are difficult to differentiate crystallographically.[20]

The synthesis and X-ray analysis[19] of the analogous bromine derivative, $[Tc(NO)Br_2(PPh_3)_2(CO)]$ **[17]**, did not fully alleviate this problem. The room temperature X-ray structure determination of **[17]** enabled the heavier Br groups to be distinguished from the NO and CO moieties; in addition, the *trans* configuration of the triphenylphosphine ligands and *cis* orientation of the carbonyl and nitrosyl groups was confirmed. However, site disorder still exists and the electronically similar NO and CO ligands still cannot be differentiated accurately enough to obtain reasonable bond distance information. Thus, the gross geometry of **[17]** is confirmed as *cis*-[Tc(NO)Br_2(PPh_3)$_2$(CO)], but quantitative comparisons with other structurally characterized nitrosyltechnetium(I) complexes[2,21,22] are not possible at this time.

Reaction of [Tc(NO)Cl_2(PPh_3)$_2$(CO)] with pyridine

The carbonyl ligand of [Tc(NO)Cl_2(PPh_3)$_2$(CO)] is labile and can be displaced by pyridine; similar reactivity with aromatic amines is seen in the mixed ligand technetium carbonyl complexes [Tc(SAr)$_3$(CO)$_2$][13,14] and [Tc($NCCH_3$)(CO)$_5$]PF_6.[23] When complex **[15]** is refluxed in pyridine, the solution darkens from yellow to orange to red within an hour, and the cherry-red trispyridine complex [Tc(NO)Cl_2(py)$_3$] **[3]** can be isolated from the reaction mixture in 69% yield. As occurs in the preparation of **[3]** from [Tc(NO)Cl_2(PPh_3)$_2$($NCCH_3$)], the high temperature conditions allow the labile carbonyl group and both triphenylphosphine ligands to be substituted. The ligand exchange reactions which lead to the synthesis of [Tc(NO)Cl_2(py)$_3$] are summarized in **Figure III-4**.

Reactions of [Tc(NO)Cl_2(PPh_3)$_2$($NCCH_3$)] with *tert*-butylisonitrile

The reactions of [Tc(NO)Cl_2(PPh_3)$_2$($NCCH_3$)] **[2]** with *tert*-butylisonitrile, summarized in **Figure III-5**, are analogous to the reactions of the starting material with pyridine and result in the formation of three new nitrosyltechnetium(I) substitution products. As seen in Chapter 2, these are reactions in which the stepwise substitution of the neutral ligands acetonitrile and triphenylphosphine can be controlled by the choice of appropriate temperature conditions and reaction stoichiometry. The integrity of the nitrosyltechnetium(I) core is maintained in all of the observed reactions.

Characterization of the isonitrile derivatives presented in this investigation includes data from elemental analysis, fast atom bombardment mass spectrometry, infrared, and technetium and proton nuclear magnetic resonance spectroscopies. Elemental analysis and mass spectral results confirm the product compositions. In addition to the expected molecular ion and fragmentation peaks, which occur due to sequential loss of the chloride and neutral ligands, each isonitrile complex also exhibits daughter peaks resulting from the cleavage of a *tert*-butyl group from an isonitrile ligand; for example, the peak at 392 m/z in the mass spectrum of $[Tc(NO)Cl_2(CNtBu)_3]$, $[Tc(NO)Cl_2(CNtBu)_2CN + H]^+$, is formed in this manner.

Data from the infrared spectra of the products confirm the presence of the linear NO^+ moiety in all cases. The nitrosyl absorbances are clustered between 1736 and 1760 cm^{-1}, in the center of the range established for linear nitrosyl ligands.[24] These bands are located at higher frequencies than was observed in the IR spectra of similar nitrosyl complexes containing aromatic amines, described in Chapter 2. Also seen in the IR spectra of the isonitrile products are prominent CN stretching vibrations, located from 2157 to 2214 cm^{-1}. These values are higher than the 2127 cm^{-1} frequency band which appears in the spectrum of free *tert*-butylisonitrile, obtained in CCl_4. This increase in the observed CN stretch occurs upon coordination of *tert*-butylisonitrile to the technetium metal ion because the isonitrile ligand bonds predominantly as a σ-donor (**Figure III-6A**) rather than as a π-acceptor ligand (**Figure III-6B**).[25-27] This is consistent with the greater π-acid capabilities of the nitrosyl ligand.[28]

Analysis of the isonitrile complexes by ^{99}Tc-NMR spectroscopy yields technetium signals in the range of -329 to -500 ppm relative to $[NH_4][^{99}TcO_4]$.

The chemical shifts of the isonitrile complexes are located farther upfield than those of the aromatic amine complexes described in Chapter 2, indicating greater shielding of the technetium nucleus.

[Tc(NO)Cl$_2$(PPh$_3$)$_2$(CNtBu)]

The monoisonitrile complex [Tc(NO)Cl$_2$(PPh$_3$)$_2$(CNtBu)] **[18]** can be prepared from a reaction between **[2]** and *tert*-butylisonitrile at room temperature; the sample must be purified by column chromatography to remove traces of the disubstitution product **[19]**. Like [Tc(NO)Cl$_2$(PPh$_3$)$_2$(NCCH$_3$)] **[2]**, [Tc(NO)Cl$_2$(PPh$_3$)$_2$(py)] **[4]** and [Tc(NO)Cl$_2$(PPh$_3$)$_2$(lut)] **[5]**, compound **[18]** is unstable in dichloromethane and cannot be stored in solution for extended periods of time. The mass spectrum of **[18]** exhibits a molecular ion peak at 806 *m/z* and numerous fragmentation peaks from loss of the chloride, isonitrile, or triphenylphosphine ligands. A solution of [Tc(NO)Cl$_2$(PPh$_3$)$_2$(CNtBu)] in 3:1 C_6D_6/CD_2Cl_2 gives a ^{99}Tc-NMR signal at -329 ppm relative to the pertechnetate standard.

Analysis of a sample of [Tc(NO)Cl$_2$(PPh$_3$)$_2$(CNtBu)] in 4:1 C_6D_6/CD_2Cl_2 by ^{1}H-NMR spectroscopy indicates two multiplets at 8.04 and 7.06 ppm in a 2:3 ratio, as expected for equivalent *trans*-triphenylphosphine ligands. While only one resonance is anticipated, two singlets are observed for the methyl groups of the isonitrile ligands. The first singlet, at 0.60 ppm, integrates to 6.4H, and the second resonance, slightly upfield at 0.56 ppm, corresponds to 2.6H. A similar ^{1}H-NMR spectrum is obtained from solutions of **[18]** in CD_2Cl_2 alone. Because the chemical shift of free *tert*-butylisonitrile occurs downfield at 0.95 ppm in 4:1 C_6D_6/CD_2Cl_2, the two singlets in the spectrum of **[18]** cannot be explained by the type of sample decomposition observed to occur in solutions of [Tc(NO)Cl$_2$(PPh$_3$)$_2$(NCCH$_3$)] **[2]**. In addition, no significant changes in the integrations of the *tert*-butylisonitrile resonances are seen in ^{1}H-NMR spectra of **[18]** taken over a four day period; solutions of **[2]**, on the other hand, show an increase in the concentration of free acetonitrile over time.

Rather than sample decomposition, the appearance of two *tert*-butylisonitrile resonances suggests the existence of isomers in solutions of **[18]**. The isomers are present in a fixed ratio, and no evidence of interconversion is observable. As there is no indication of triphenylphosphine ligand inequivalence in the ^{1}H-NMR spectrum of **[18]**, isomers in which the *tert*-butylisonitrile ligand is positioned either *cis* or *trans* to the nitrosyl are predicted (**Figure III-7**).

Data obtained using infrared spectroscopy confirm the existence of *cis*/*trans* isomers of $[Tc(NO)Cl_2(PPh_3)_2(CNtBu)]$ in the solid state as well as in solution. Like $[Tc(NO)Cl_2(PPh_3)_2(py)]$ **[4]**, the IR spectrum of **[18]** in KBr shows two bands attributable to the nitrosyl stretching vibration where only one band should be observed (**Figure III-8**). A band of medium intensity is located at 1703 cm^{-1}, and a very strong band is found at 1737 cm^{-1}; the CN stretch appears at 2171 cm^{-1} in this spectrum.

$[Tc(NO)Cl_2(PPh_3)(CNtBu)_2]$

The disubstitution product $[Tc(NO)Cl_2(PPh_3)(CNtBu)_2]$ **[19]** can be synthesized from complex **[2]** and excess *tert*-butylisonitrile in a refluxing dichloromethane solution. Although the higher reaction temperatures and greater ligand concentration favor the formation of the pale yellow complex **[19]**, traces of the monosubstitution product **[18]** can be found in the reaction mixture and must be removed by column chromatography. The molecular ion peak, located at 627 *m/z* in the mass spectrum (**Figure III-9**), confirms the formulation of the complex as $[Tc(NO)Cl_2(PPh_3)(CNtBu)_2]$. The IR spectrum displays two strong isonitrile CN stretches of equal intensity, located at 2200 and 2168 cm^{-1}, caused by inequivalent isonitriles. This *cis* ligand configuration is confirmed by the ^{1}H-NMR spectrum of **[19]**, which shows two distinct resonances from the methyl groups of the *tert*-butylisonitrile ligands; the singlets are located at 1.59 and 1.29 ppm and integrate in a 1:1 ratio. The geometry of complex **[19]** appears to be directly analogous to the assigned *cis*-pyridine ligand configuration of [$Tc(NO)Cl_2(PPh_3)(py)_2$] **[6]** (Chapter 2) and the previously synthesized rhenium analog [$Re(NO)Cl_2(PPh_3)(CNtBu)_2$].[17]

The bisisonitrile complex exhibits a ^{99}Tc-NMR signal at -380 ppm. This chemical shift is located farther upfield than the signal of the monoisonitrile complex **[18]**, indicating a greater amount of shielding in complex **[19]**.

[$Tc(NO)X_2(CNtBu)_3$] (X is Cl or Br)

When the reaction between [$Tc(NO)Cl_2(PPh_3)_2(NCCH_3)$] **[2]** and excess *tert*-butylisonitrile is performed at higher temperatures, the yellow complex [$Tc(NO)Cl_2(CNtBu)_3$] **[20]** can be isolated in 68% yield after chromatographic purification. As with the other isonitrile complexes, a prominent molecular ion peak is observed in the mass spectrum of **[20]** at 448 *m/z*, and characteristic peaks appear due to loss of the Cl (413 *m/z*), *t*-butyl (392 *m/z*), and CNtBu (367 *m/z*) fragments, among others (**Figure III-10**). A strong ^{99}Tc-NMR signal is located at -498 ppm from the shielded technetium nucleus of **[20]**.

The complex gives a very simple ^{1}H-NMR spectrum which consists of two singlets that integrate in a 2:1 ratio and are located at 1.58 and 1.56 ppm, respectively. The resonance at lower field results from two equivalent isonitriles positioned *trans* to each other, whereas the unique isonitrile ligand gives rise to the higher field signal at 1.56 ppm.

Analysis of the IR spectrum of [$Tc(NO)Cl_2(CNtBu)_3$] in chloroform shows a very strong, broad nitrosyl stretch at 1760 cm^{-1} and two CN stretches, a medium intensity band at 2214 cm^{-1} and a very strong absorbance at 2188 cm^{-1}. Based on analogy with *mer*-[Tc(NO)Br_2(CNtBu)$_3$],[2] the higher frequency band of medium intensity is assigned to the unique *tert*-butylisonitrile ligand.

The bromine derivative [Tc(NO)Br_2(CNtBu)$_3$] **[21]** was prepared in order to allow direct comparisons between the pale purple complex *mer*-[Tc(NO)Br_2(CNtBu)$_3$], prepared by Linder,[2] and the yellow material **[21]** obtained from compound **[16]** in the manner described in this investigation. The characterization of complex **[21]** correlates directly with the data obtained from its chlorine analog **[20]**; the IR spectrum of **[21]** is shown in **Figure III-11**. As was observed with the carbonyl complexes **[15]** and **[17]**, the ^{99}Tc-NMR spectrum of the bromine derivative differs slightly from that of the chlorine complex due to greater shielding of the technetium nucleus by bromine.

Although both are formulated as [Tc(NO)Br_2(CNtBu)$_3$], the yellow complex presented here differs considerably from Linder's purple compound *mer*-[Tc(NO)Br_2(CNtBu)$_3$]. The differences in the IR and ^{1}H-NMR spectra of the two complexes are summarized in **Table III-1**. The isonitrile CN stretches of **[21]** in dichloromethane are more closely spaced and differ from those of the purple complex by 10 - 20 cm^{-1}; however, no significant difference in the positions of the two NO stretching vibrations is seen. The *tert*-butylisonitrile resonances found in the ^{1}H-NMR spectrum of the yellow complex **[21]** are shifted 0.11 - 0.13 ppm downfield from those of *mer*-[Tc(NO)Br_2(CNtBu)$_3$]. These spectral deviations are greater than the estimated experimental error associated with each instrument. The observed spectral differences indicate that the yellow and purple complexes are not identical in structure but are geometric isomers.

The structure of the purple complex *mer*-[Tc(NO)Br_2(CNtBu)$_3$] was determined[2] by X-ray crystallography and is pictured in **Figure III-12**. The *tert*-butylisonitrile ligands of the purple complex are positioned in a meridional fashion, *trans* to the nitrosyl group. The yellow complex **[21]** may be related to *mer, trans*-[Tc(NO)Br_2(CNtBu)$_3$] as the isomer in which the isonitrile ligands are facially coordinated (**Figure III-13A**) or as the *mer, cis* isomer (**Figure III-13B**). The latter geometry is more likely based on comparisons with the structurally characterized trispyridine complex *mer, cis*-[Tc(NO)Cl_2(py)$_3$] **[3]** (Chapter 2), which is also synthesized from **[2]**. Because a *cis* orientation of the π-acceptor ligands NO and CNtBu is thermodynamically favored, a facial geometry is not expected in **[21]** due to its lower stability. It is surprising, therefore, that the purple complex contains a *tert*-butylisonitrile ligand coordinated *trans* to the nitrosyl. This isomer most likely represents the kinetic reaction product; its thermodynamic instability may account for the low (32%) product yield observed[2] in the reaction of [Tc(NO)Br_4]$^-$ and *tert*-butylisonitrile. It is interesting that no such difference in product geometry is seen in the synthesis of [Tc(NO)Cl_2(py)$_3$] **[3]** from n-Bu_4N[Tc(NO)Cl_4] and pyridine; the recrystallized material isolated from the reaction is spectroscopically identical to the product obtained from the reaction of pyridine with [Tc(NO)Cl_2(PPh_3)$_2$($NCCH_3$)] **[2]**.

Summary

The acetonitrile ligand of [Tc(NO)X_2(PPh_3)$_2$($NCCH_3$)] can be selectively displaced by carbon monoxide to form [Tc(NO)X_2(PPh_3)$_2$(CO)] (X is Cl or Br). Partial characterization of the bromine derivative [Tc(NO)Br_2(PPh_3)$_2$(CO)] **[17]** by X-ray crystallography indicates a *cis* orientation of NO and CO ligands. The lability of the neutral ligands of [Tc(NO)Cl_2(PPh_3)$_2$(CO)] **[15]** is utilized to prepare the trispyridine complex [Tc(NO)Cl_2(py)$_3$] **[3]**. Substitution reactions of [Tc(NO)Cl_2(PPh_3)$_2$($NCCH_3$)] **[2]** with the π-acceptor ligand *tert*-butylisonitrile are analogous to the reactions of [2] with aromatic amines and produce $[Tc(NO)Cl_2(PPh_3)_2(CNtBu)]$ [18], $[Tc(NO)Cl_2(PPh_3)(CNtBu)_2]$ [19], or $[Tc(NO)Br_2(CNtBu)_3]$ [20], depending on the reaction temperature and ligand concentration. Since substitution of the neutral ligands acetonitrile and triphenylphosphine was shown to be successful, exchange reactions involving the chloride ligands were attempted and are the subject of the next chapter.

References

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10. It has previously been reported[11] by our laboratories that, although samples analyze well for other elements, carbon analyses are often up to one carbon low. A possible explanation is that an incomplete combustion of the complex leads to the formation of residual technetium carbide.

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Table III-1. A Comparison of IR and ^{1}H-NMR data for $[Tc(NO)Br_2(CNtBu)_3]$ **[21]** and *mer, trans*-$[Tc(NO)Br_2(CNtBu)_3]$[2] **[KL]**.

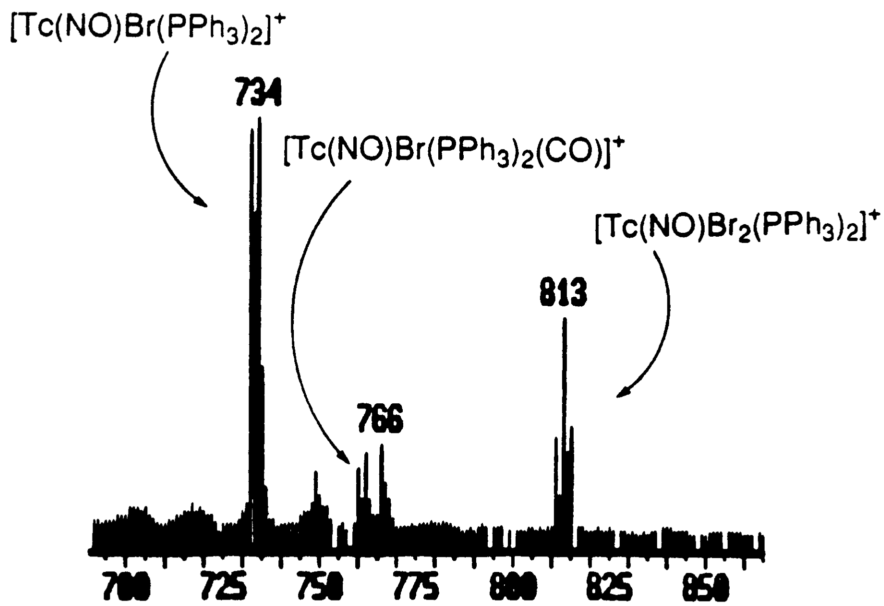
	[21]	**[KL]**
Color	yellow	purple
IR (KBr) (cm^{-1}):	ν (NO) 1748 (vs)	ν (NO) 1755 (vs)
	1734 (vs)	
	ν (CN) 2214 (m)	ν (CN) 2230 (m)
	2182 (vs)	2160 (s)
IR (CH_2Cl_2):	ν (NO) 1760 (vs)	ν (NO) 1762 (vs)
	ν (CN) 2214 (w)	ν (CN) 2235 (m)
	2185 (vs)	2175 (vs)
^{1}H-NMR (CD_2Cl_2) (ppm):	1.58 (s, 2H)	1.47 (s, 2H)
	1.56 (s, 1H)	1.43 (s, 1H)
Reference	this work	2

Figure III-1. Schematic representation of the preparation of $[Tc(NO)X_2(PPh_3)_2(CO)]$ (X is Cl or Br).

$$[Tc(NO)X_2(PPh_3)_2(NCCH_3)] \quad + \quad CO_{(g)} \quad \xrightarrow[\text{R.T.}]{CHCl_3,\text{ 3 hrs.}} \quad [Tc(NO)X_2(PPh_3)_2(CO)]$$

X = Cl or Br

Figure III-2. Fast atom bombardment mass spectrum (+) of $[Tc(NO)Br_2(PPh_3)_2(CO)]$ **[17]**.



[Tc(NO)Br(PPh3)2]+
734
[Tc(NO)Br(PPh3)2(CO)]+
[Tc(NO)Br2(PPh3)2]+
813
766
700
725
750
775
800
825
850

Figure III-3. Proposed geometry of $[Tc(NO)Br_2(PPh_3)_2(CO)]$ **[17]**.

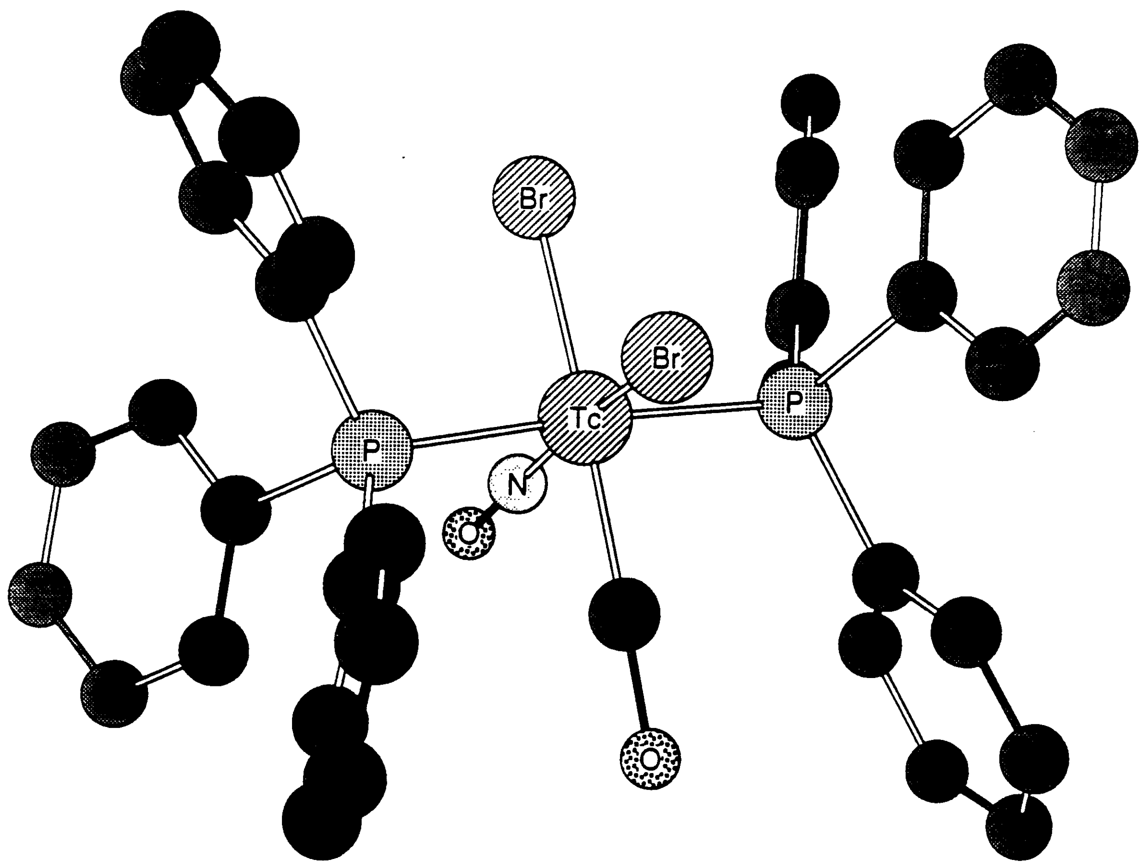
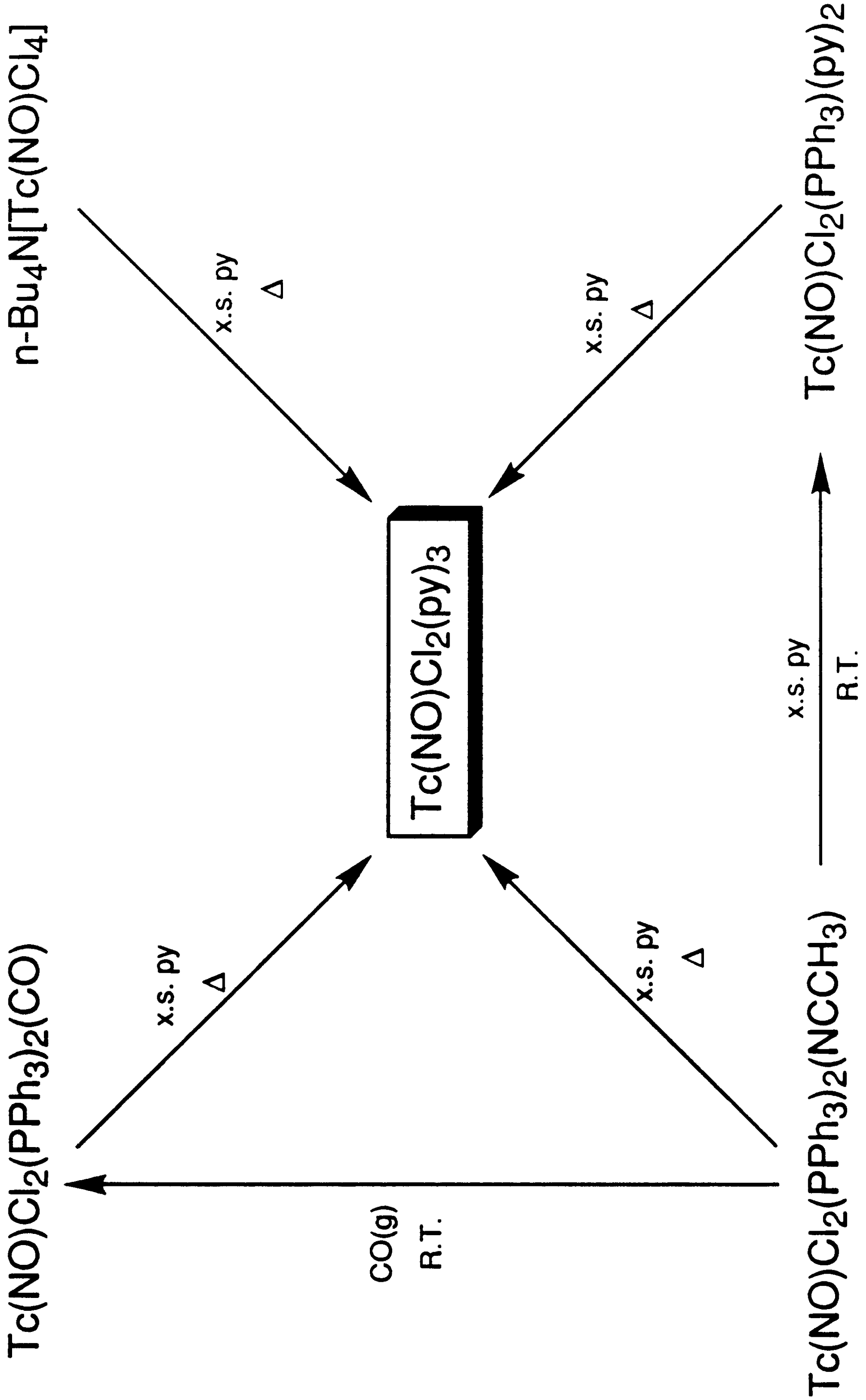
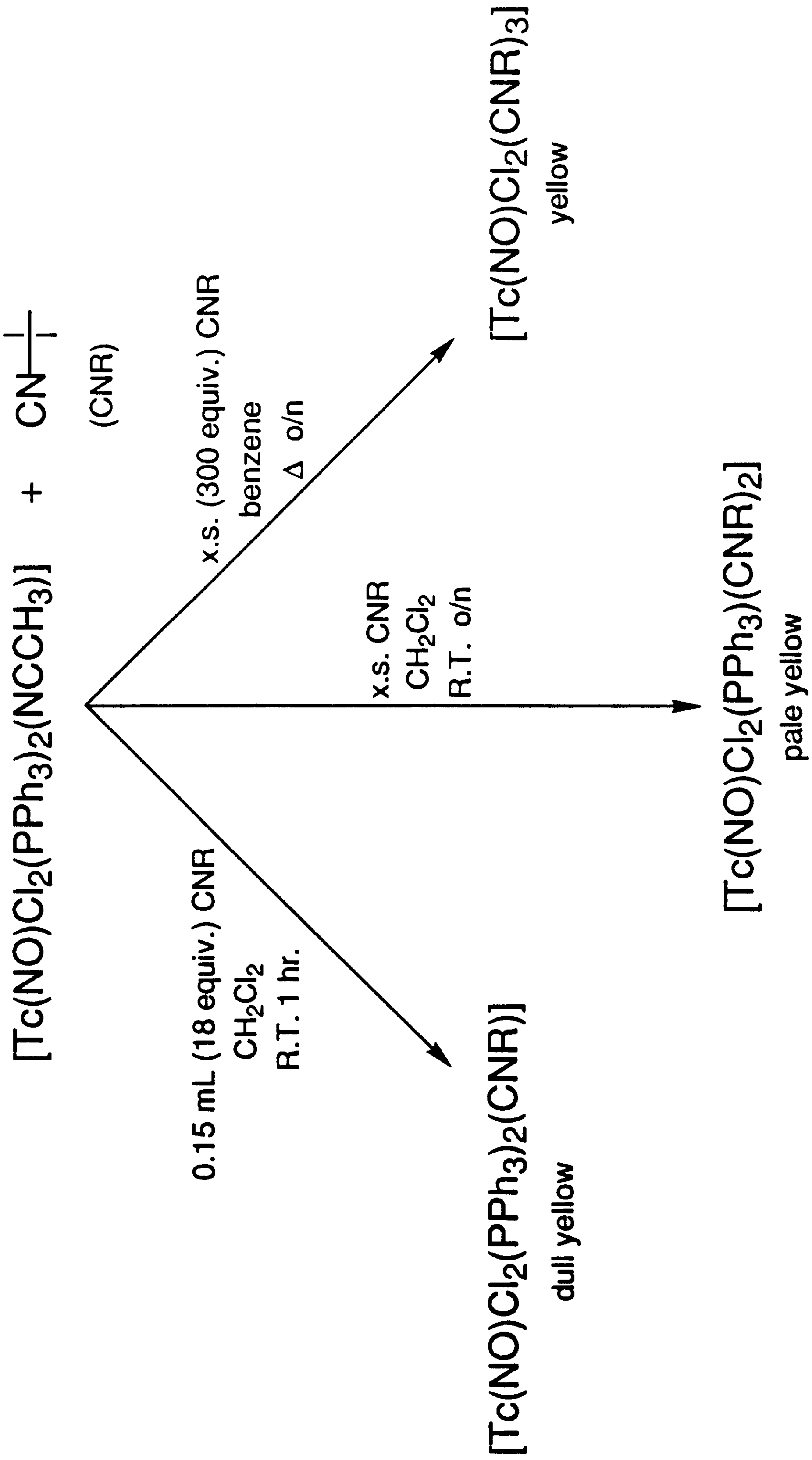

Br
Br
Tc
P
P
N
O
O

Figure III-4. Schematic representation of the synthetic routes available in the preparation of $[Tc(NO)Cl_2(py)_3]$ **[3]**.



n-Bu4N[Tc(NO)Cl4]
Tc(NO)Cl2(PPh3)(py)2
x.s. py
Δ
x.s. py
Δ
Tc(NO)Cl2(py)3
x.s. py
R.T.
Tc(NO)Cl2(PPh3)2(CO)
x.s. py
Δ
x.s. py
Δ
CO(g)
R.T.
Tc(NO)Cl2(PPh3)2(NCCH3)

Figure III-5. Scheme for the reactions of $[Tc(NO)Cl_2(PPh_3)_2(NCCH_3)]$ **[2]** with *tert*-butylisonitrile.

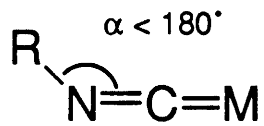


[Tc(NO)Cl2(PPh3)2(NCCH3)] + CN— (CNR)
0.15 mL (18 equiv.) CNR
CH2Cl2
R.T. 1 hr.
x.s. CNR
CH2Cl2
R.T. o/n
x.s. (300 equiv.) CNR
benzene
Δ o/n
[Tc(NO)Cl2(PPh3)2(CNR)]
dull yellow
[Tc(NO)Cl2(PPh3)(CNR)2]
pale yellow
[Tc(NO)Cl2(CNR)3]
yellow

Figure III-6. Diagram depicting the binding of the isocyanide molecule CNR to a metal ion M as a σ-donor ligand (**A**) or as a π-accepting ligand (**B**).

A.

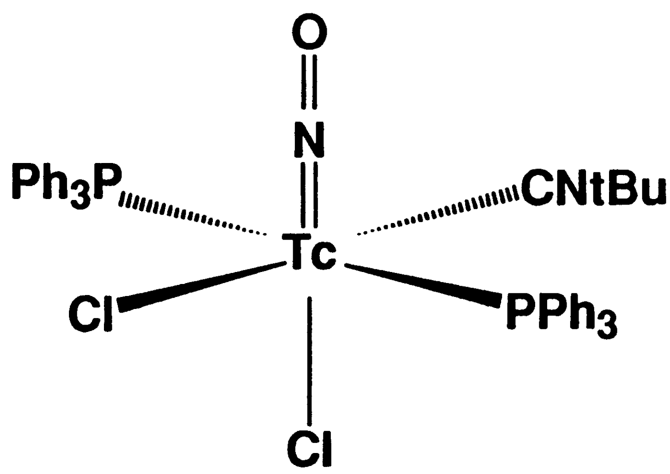
σ-donor ligand



B.

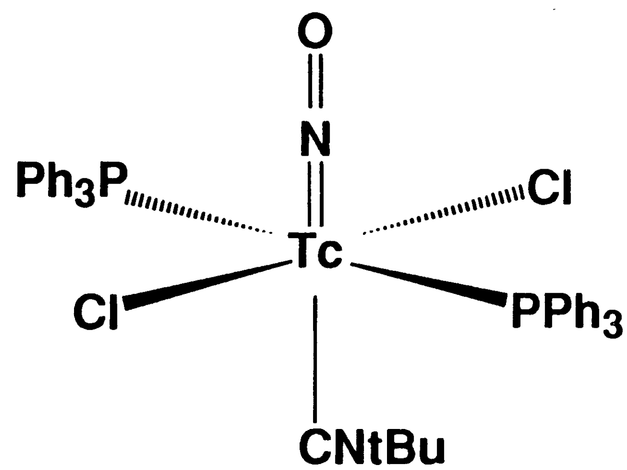
π-accepting ligand

Figure III-7. Proposed *cis* (**A**) and *trans* (**B**) isomers of $[Tc(NO)Cl_2(PPh_3)_2(CNtBu)]$ **[18]**.



A.

cis-geometry



B.

trans-geometry

Figure III-8. Infrared spectrum of $[Tc(NO)Cl_2(PPh_3)_2(CNtBu)]$ [18] taken in KBr.

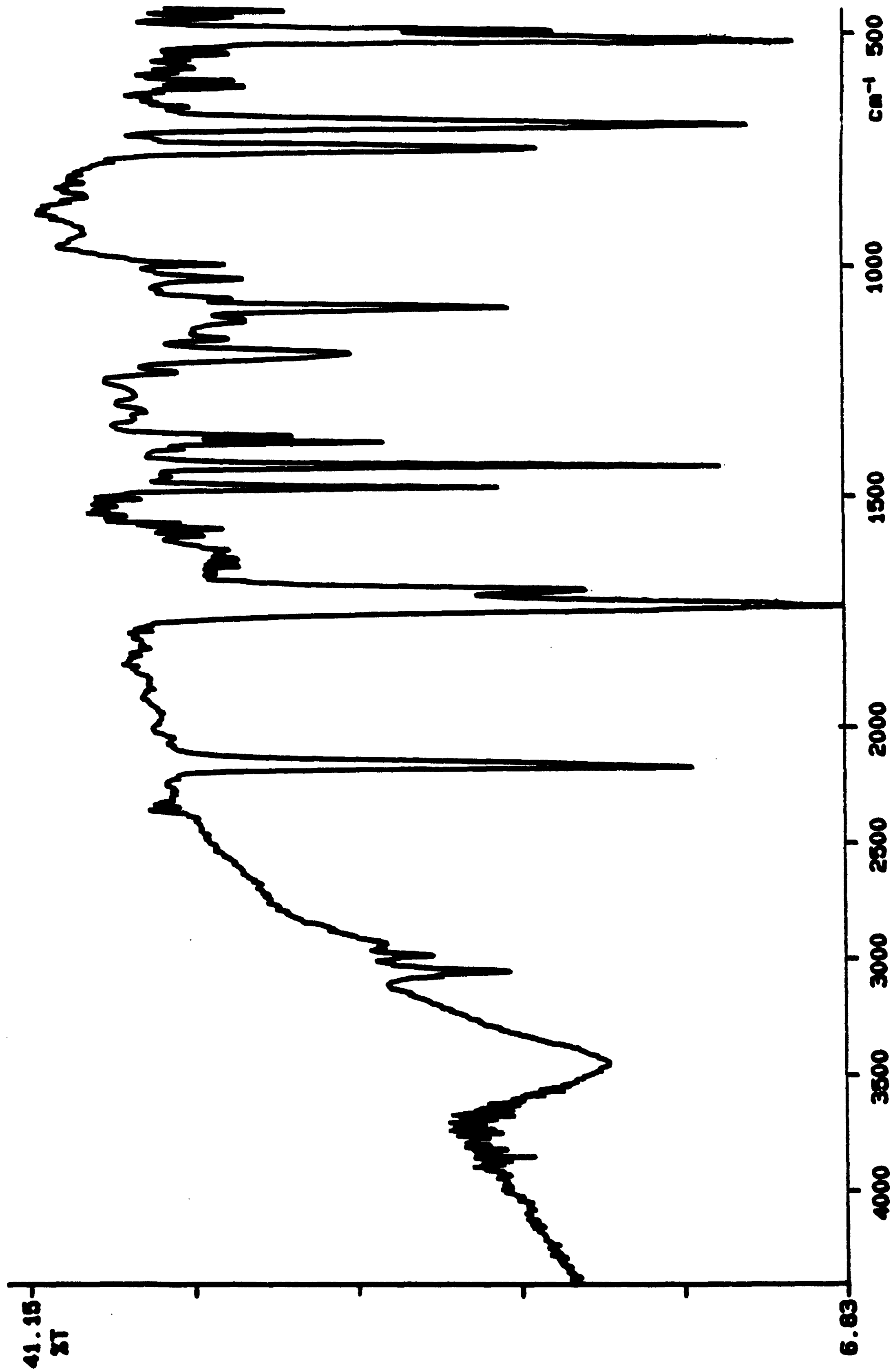
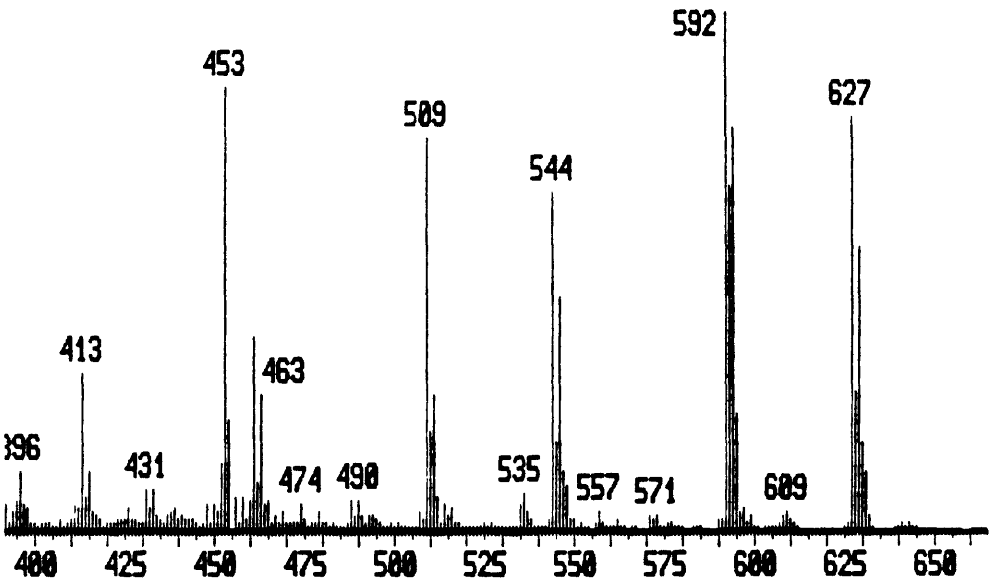
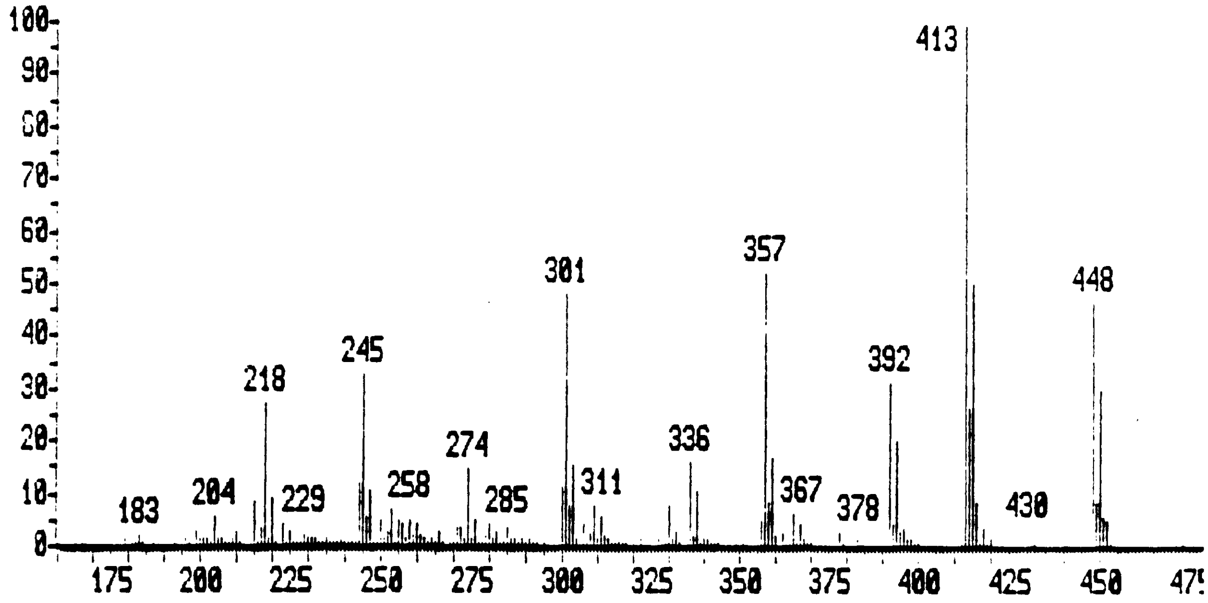

41.15
%T
6.83
cm-1
500
1000
1500
2000
2500
3000
3500
4000

Figure III-9. Fast atom bombardment mass spectrum (+) of $[Tc(NO)Cl_2(PPh_3)(CNtBu)_2]$ **[19]**.



396
413
431
453
463
474
490
509
535
544
557
571
592
609
627
400
425
450
475
500
525
550
575
600
625
650

Figure III-10. Fast atom bombardment mass spectrum (+) of $[Tc(NO)Cl_2(CNtBu)_3]$ **[20]**.



100
90
80
70
60
50
40
30
20
10
0
183
204
218
229
245
258
274
285
301
311
336
357
367
378
392
413
430
448
175
200
225
250
275
300
325
350
375
400
425
450
475

Figure III-11. Infrared spectrum of $[Tc(NO)Br_2(CNtBu)_3]$ **[21]** obtained in KBr.

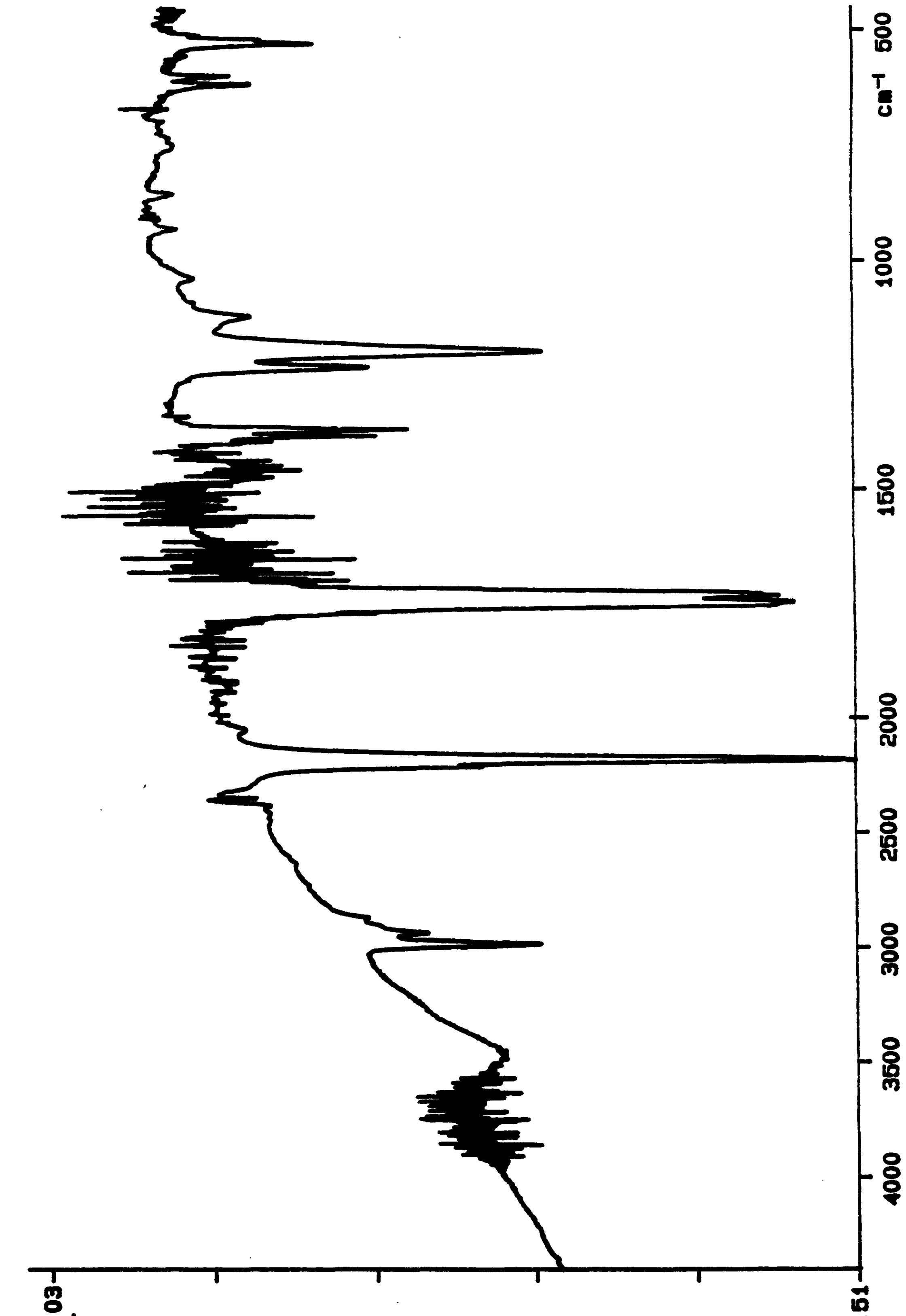

47.03
%T
1.51
cm⁻¹
500
1000
1500
2000
2500
3000
3500
4000

Figure III-12. Structure of *mer, trans*-$[Tc(NO)Br_2(CNtBu)_3]$[2] showing the atom-labelling scheme and 30% probability thermal ellipsoids.

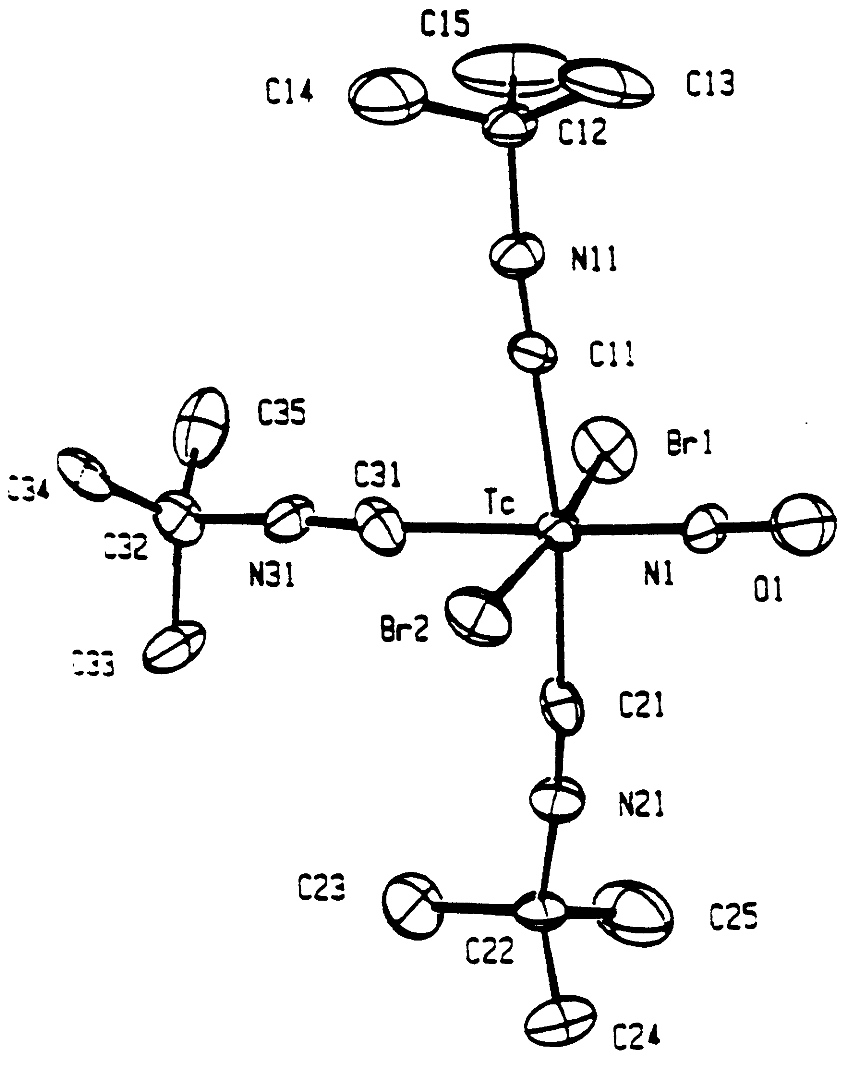
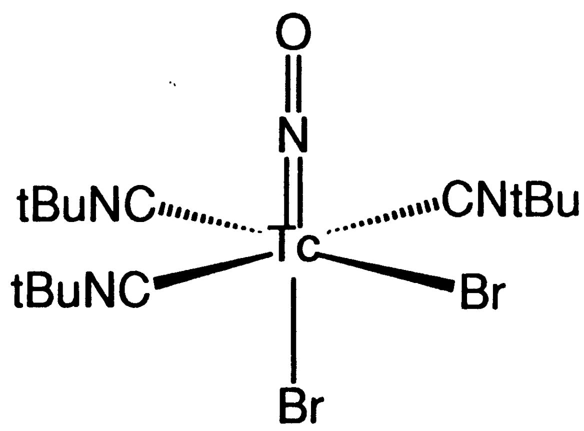
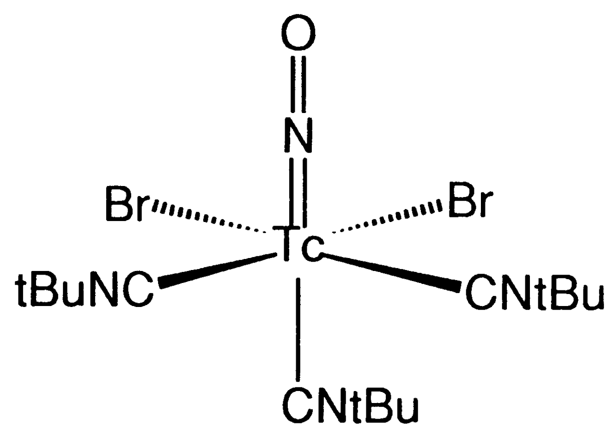

C15
C14
C13
C12
N11
C11
C35
Br1
C34
C31
Tc
C32
N31
N1
O1
Br2
C33
C21
N21
C23
C22
C25
C24

Figure III-13. Possible isomers of the yellow complex $[Tc(NO)Br_2(CNtBu)_3]$ **[21]**.



A.

mer, cis-geometry



B.

fac-geometry

CHAPTER IV

The Synthesis of Nitrosyl Complexes of Technetium with Sulfur-Containing Cores

Introduction

While interest in the preparation of technetium complexes with thiolate ligands has increased in recent years,[1,2] the chemistry of technetium nitrosyl and thionitrosyl derivatives with sulfur ligands is still largely unexplored. The technetium(III) complex [$Tc(NO)Cl(SC_{10}H_{13})_3$], formed in the reaction of n-$Bu_4N[Tc(NO)Cl_4]$ with the sterically hindered arenethiolate 2,3,5,6-tetramethylbenzenethiol, is the only known nitrosyl complex containing sulfur ligation.[3] Likewise, the dithiocarbamate derivative [$Tc(NS)(S_2CNEt_2)_2X_2$] (X is Cl or Br) is the one characterized thionitrosyl representative.[4,5] Given the ease of ligand exchange demonstrated by the mixed ligand nitrosyl complex [$Tc(NO)Cl_2(PPh_3)_2(NCCH_3)$] **[2]** in reactions with aromatic amines and π-acceptors, one would predict the preparation of sulfur-containing nitrosyl complexes from this versatile starting material to be straightforward.

The sulfur ligands used in this study are pictured in **Figure IV-1**. The alkyl xanthate ligand (**Figure IV-1A**) was first used in technetium chemistry as an extraction agent in the separation of technetium from rhenium.[6,7] Since that time, its chemistry with technetium has been more rigorously detailed,[1,8,9] and xanthate complexes in the series [$Tc(PPh_3)(S_2COR)_3$] have been examined with regards to use in nuclear medicine.[10] The chemistry of the closely related dithiocarbamate ligand, NaS_2CNR_2, has been studied extensively in both technetium[8,9,11] and rhenium[12-15] systems, and it has proven to be a good agent for ligand exchange; by analogy, the chemistry of the xanthate ligand should be as rich. The second sulfur-based ligand used in this study, 2-mercaptopyridine (**Figure IV-1B**), was studied previously in reactions with nitrosyltechnetium derivatives, but no well-defined complexes were isolated.[16]

It is anticipated that the behavior of 2-mercaptopyridine and alkyl xanthate in ligand substitution reactions with $[Tc(NO)Cl_2(PPh_3)_2(NCCH_3)]$ will be analogous. In addition, chloride displacement in **[2]** should follow the substitution patterns established by the reactions of $[ReCl_3(PPh_3)_2(NCCH_3)]$ with anionic ligands.[15,17] These exchange reactions highlight the advantages in using starting materials such as $[Tc(NO)Cl_2(PPh_3)_2(NCCH_3)]$, which possesses three ligands with different substitutional capabilities, in the rational synthesis of mixed ligand technetium complexes with targeted properties.

Experimental Section

Caution: Technetium-99 is a weak β^- emitter (E=292 keV, $t_{1/2}$= 2.12 x 10^5 years). All manipulations of solutions and solids were performed in laboratories approved for the use of low-level radioactivity, following precautions detailed elsewhere.[18]

Ammonium pertechnetate was obtained as a gift from Du Pont Merck Pharmaceutical Company. The starting material, $[Tc(NO)Cl_2(PPh_3)_2(NCCH_3)]$ **[2]**, was synthesized as described in Chapter 1. The potassium xanthate ligands [$K(S_2COR)$, where R is the neopentyl (nPe), isobutyl (iBu), or methyl (Me) group] were synthesized according to the method of Shupe,[19] and 2-mercaptopyridine (HSpy) and 1,1,3,3-tetramethylguanidine were obtained from Aldrich Chemical Company. Solvents were of at least reagent grade; solvents and reagents were used as received unless otherwise indicated. Column chromatography was performed with ICN Biomedicals Alumina N, Activity I.

Fast atom bombardment mass spectra (FABMS) were recorded with a MAT 731 mass spectrometer equipped with an Ion Tech B11N FAB gun that produced a beam of 6-8 keV Xenon neutrals. The samples were dissolved in a *p*-nitrobenzyl alcohol matrix. Peaks resulting from the most abundant isotope of chlorine, ^{35}Cl, are referenced in the mass spectra. Routine infrared spectra were recorded on a Mattson Cygnus 100 FT spectrophotometer or on a Perkin-Elmer 1600 Series FTIR. ^1H and ^{99}Tc NMR spectra were recorded at room temperature using a Varian XL-300 MHz spectrometer. The primary reference for ^{99}Tc-NMR, $[NH_4][^{99}TcO_4]$ in D_2O, resonates at 67.516 MHz and is designated as 0 ppm. A 34-μs pulse width (90° tip) and 0.15-s acquisition time were used. No additional relaxation delay was employed. For differences greater than the maximum spectral width (10^5 Hz, 1480 ppm) obtainable, chemical shifts could be calculated based on the spectrometer frequency, transmitter offset, transmitter base offset, and relative shift within the spectral window. We estimate that the error associated with these values is ±2 ppm. The presence of spectral folding or other artifacts was ruled out by changing the transmitter offset by a known frequency and verifying that the resonance moved within the spectral window by the appropriate amount and in the expected direction.[20] Two-dimensional homonuclear shift correlation experiments were performed on a Varian Unity-300 spectrometer using the COSY macro and the following parameters: D1=1.000 s, NP=1024, NI=128, FN1=1024. The spectral width was minimized, double precision was not employed, and the raw data was symmetrized using the FOLDT command. Elemental analyses were performed by Atlantic Microlab Inc., Norcross, GA.

Preparation of [chloro(isobutylxanthate)nitrosylbis(triphenylphosphine) technetium(I)], [Tc(NO)Cl(PPh_3)$_2$(S_2COiBu)] [22].

A methanolic solution (8 mL) of potassium isobutylxanthate (11.4 mg, 0.061 mmol) was added to a solution of [Tc(NO)Cl_2(PPh_3)$_2$($NCCH_3$)] **[2]** (40.0 mg, 0.052 mmol) in dichloromethane (8 mL), and the mixture was refluxed overnight to form an orange solution. After cooling to room temperature, the solution was filtered through cotton to remove traces of a white precipitate (KCl) and concentrated to 4 mL by rotary evaporation. As the sample volume was reduced, a bright yellow solid precipitated from the solution. The product was collected on a fritted glass funnel, rinsed with distilled, deionized water (10 mL) and pentane (10 mL), and dried in vacuo. Yield 22.4 mg (51.4%) of the bright yellow product [Tc(NO)Cl(PPh_3)$_2$(S_2COiBu)].

Anal. Calcd for $C_{41}H_{39}ClNO_2P_2S_2Tc$: C, 58.71; H, 4.65; Cl, 4.18; S, 7.64.

Found: C, 58.43; H, 4.77; Cl, 4.36; S, 7.88.

FABMS(+) (*m/z*): 837 [Tc(NO)Cl(PPh_3)$_2$(S_2COiBu)]$^+$,

802 [Tc(NO)(PPh_3)$_2$(S_2COiBu)]$^+$, 688 [Tc(NO)Cl(PPh_3)$_2$]$^+$,

575 [Tc(NO)Cl(PPh_3)(S_2COiBu)]$^+$, 540 [Tc(NO)(PPh_3)(S_2COiBu)]$^+$.

IR (KBr) (cm^{-1}): ν (NO) 1702 (vs).

ν (CS) 1238 (vs, br).

^{1}H-NMR (CD_2Cl_2): δ=7.40 (m, 18H), 7.33 (m, 13H), 4.22 (d, 2H), 2.06 (heptet, 1H), 0.96 (d, 6H).

^{99}Tc-NMR (CD_2Cl_2): δ=3.5 ppm, linewidth 2230 Hz (δ TcO_4^- is 0 ppm).

Preparation of [chloro(2-mercaptopyridine)nitrosylbis(triphenylphosphine) technetium(I)], [Tc(NO)Cl(PPh_3)$_2$(Spy)] [23].

To an orange solution of **[2]** (95.2 mg, 0.124 mmol) and 2-mercaptopyridine (28.6 mg, 0.26 mmol) in dichloromethane (15 mL) was added approximately 75 μL of 1,1,3,3-tetramethylguanidine. This addition caused the solution to darken immediately to a wine red color. The sample was refluxed overnight, and no further color change was observed. The solution was concentrated to 1 mL under reduced pressure and chromatographed on an alumina column conditioned and eluted with dichloromethane. A purple-red band was collected, concentrated to 4 mL, and layered with excess pentane (40 mL). The mixture was refrigerated overnight to yield a lilac-purple precipitate.

The solid was collected on a fritted glass funnel, rinsed with pentane (10 mL), and dried in vacuo. Yield 24.0 mg (24.3%).

Anal. Calcd for $C_{41}H_{34}ClN_2OP_2STc$: C, 61.65; H, 4.26; Cl, 4.39; S, 4.01.

Found: C, 61.42; H, 4.30; Cl, 4.52; S, 4.11.

FABMS(+) (*m/z*): 798 $[Tc(NO)Cl(PPh_3)_2(Spy)]^+$, 763 $[Tc(NO)(PPh_3)_2(Spy)]^+$, 688 $[Tc(NO)Cl(PPh_3)_2]^+$, 536 $[Tc(NO)Cl(PPh_3)(Spy)]^+$, 501 $[Tc(NO)(PPh_3)(Spy)]^+$.

IR (KBr) (cm^{-1}): ν (NO) 1696 (vs, br).

^{1}H-NMR (CD_2Cl_2): δ=7.59 (m, 12H), 7.29 (m, 19H), 6.73 (m, 2H), 6.03 (d of d, 1H), 5.65 (t of d, 1H).

^{99}Tc-NMR (CD_2Cl_2): δ=657 ppm, linewidth 8680 Hz (δ TcO_4^- is 0 ppm).

Preparation of [bis(neopentylxanthate)nitrosyltriphenylphosphine technetium(I)], $[Tc(NO)(PPh_3)(S_2COnPe)_2]$ [24].

A methanolic solution (8 mL) of potassium neopentylxanthate (53.2 mg, 0.26 mmol) was added to a solution of **[2]** (59.2 mg, 0.077 mmol) in dichloromethane (8 mL), and the mixture was refluxed overnight. The solution color turned bright orange and a white precipitate (KCl) formed as the reaction progressed. The solution was cooled to room temperature, filtered through a cotton plug, then dried completely to form an orange residue. The desired product was extracted into a solution of diethyl ether (25 mL) and pentane (10 mL) with vigorous stirring over a two hour period. The orange solution was removed, concentrated to 10 mL under reduced pressure, filtered, then dried completely to form an orange oil. The sample was taken up in acetone (5 mL) and layered with methanol (3 mL); distilled, deionized water (approximately 4 mL) was added until the solution clouded slightly. Refrigeration of this mixture resulted in the precipitation of a dark red-orange solid. The mother liquor was removed, and the solid was rinsed with water (10 mL) and methanol (10 mL) then dried in vacuo. Yield 43.9 mg (79.5%) of the bright red-orange product $[Tc(NO)(PPh_3)(S_2COnPe)_2]\cdot0.5\ C_3H_6O$.

Anal. Calcd for $C_{31.5}H_{40}NO_{3.5}PS_4Tc$: C, 50.67; H, 5.36; N, 1.88; S, 17.16.

Found: C, 50.68; H, 5.25; N, 2.06; S, 16.74.

FABMS(+) (*m/z*): 717 $[Tc(NO)(PPh_3)(S_2COnPe)_2]^+$,

587 $[Tc(NO)(PPh_3)(S_2COnPe)SH]^+$, 554 $[Tc(NO)(PPh_3)(S_2COnPe)]^+$,

456 $[Tc(NO)(S_2COnPe)_2]^+$, 423 $[Tc(NO)(PPh_3)S]^+$.

IR (KBr) (cm^{-1}): ν (NO) 1699 (vs).

ν (CS) 1229 (vs, br).

^{1}H-NMR (CD_2Cl_2): δ=7.54 (m, 6H), 7.41 (m, 9H), 4.32 (d, 2H), 3.76 (q, 2H), 2.12 (acetone), 1.06 (s, 9H), 0.86 (s, 9H).

^{99}Tc-NMR (CD_2Cl_2): δ=271 ppm, linewidth 2850 Hz (δ TcO_4^- is 0 ppm).

Preparation of [bis(isobutylxanthate)nitrosyltriphenylphosphine technetium(I)], $[Tc(NO)(PPh_3)(S_2COiBu)_2]$ [25].

This compound was prepared analogously to **[24]**, substituting potassium isobutylxanthate for potassium neopentylxanthate. Yield 43.8 mg (57.8%) of the bright red-orange product $[Tc(NO)(PPh_3)(S_2COiBu)_2]\cdot0.5\ C_3H_6O$.

Anal. Calcd for $C_{29.5}H_{36}NO_{3.5}PS_4Tc$: C, 49.32; H, 5.01; N, 1.95; S, 17.82.

Found: C, 49.66; H, 4.86; N, 2.03; S, 18.01.

FABMS(+) (*m/z*): 689 $[Tc(NO)(PPh_3)(S_2COiBu)_2]^+$,

573 $[Tc(NO)(PPh_3)(S_2COiBu)SH]^+$, 540 $[Tc(NO)(PPh_3)(S_2COiBu)]^+$,

423 $[Tc(NO)(PPh_3)S]^+$.

IR (KBr) (cm^{-1}): ν (NO) 1701 (vs).

ν (CS) 1244 (vs, br).

^{1}H-NMR (CD_2Cl_2): δ=7.54 (m, 6H), 7.41 (m, 9H), 4.42 (d, 2H), 3.88 (m, 2H), 2.19 (heptet, 1H), 2.12 (acetone), 1.86 (heptet, 1H), 1.04 (d, 6H), 0.86 (d, 6H).

^{99}Tc-NMR (CD_2Cl_2): δ=278 ppm, linewidth 2605 Hz (δ TcO_4^- is 0 ppm).

Preparation of [bis(methylxanthate)nitrosyltriphenylphosphinetechnetium(I)], $[Tc(NO)(PPh_3)(S_2COMe)_2]$ [26].

This complex was prepared analogously to **[24]**, substituting potassium methylxanthate for potassium neopentylxanthate. Yield 27.1 mg (43.9%) of the bright red-orange solid $[Tc(NO)(PPh_3)(S_2COMe)_2]\cdot C_3H_6O$.

Anal. Calcd for $C_{25}H_{27}NO_4PS_4Tc$: C, 45.25; H, 4.07; N, 2.11; S, 19.31.

Found: C, 45.31; H, 3.73; N, 2.22; S, 20.39.

FABMS(+) (*m/z*): 605 $[Tc(NO)(PPh_3)(S_2COMe)_2]^+$,

531 $[Tc(NO)(PPh_3)(S_2COMe)SH]^+$, 499 $[Tc(NO)(PPh_3)(S_2COMe) + H]^+$,

342 $[Tc(NO)(S_2COMe)_2 - H]^+$.

IR (KBr) (cm^{-1}): ν (NO) 1701 (vs).

ν (CS) 1233 (vs, br).

^{1}H-NMR (CD_2Cl_2): δ=7.55 (m, 6H), 7.41 (m, 9H), 4.24 (s, 3H), 3.76 (s, 3H), 2.12 (acetone).

^{99}Tc-NMR (CD_2Cl_2): δ=285 ppm, linewidth 2230 Hz (δ TcO_4^- is 0 ppm).

Preparation of [bis(2-mercaptopyridine)nitrosyl(triphenylphosphine) technetium(I)], [Tc(NO)(PPh_3)($Spy)_2$] [27].

A methanolic solution (15 mL) of 2-mercaptopyridine (52.5 mg, 0.47 mmol) was added to a solution of **[2]** (46.7 mg, 0.061 mmol) in dichloromethane (2 mL). Addition of approximately 150 μL of 1,1,3,3-tetramethylguanidine caused the solution to darken from orange to a ruby red color within minutes. The ruby solution was refluxed for twenty-four hours, after which time it was concentrated to 1.5 mL under reduced pressure and chromatographed on an alumina column conditioned and washed with pentane (150 mL). A red band was eluted with a 50% (v/v) acetone/pentane solution. The red fraction was filtered and the solvent was removed by rotary evaporation. The resulting dark red residue was dissolved in acetone (4 mL) and a solution of sodium tetraphenylborate (41.7 mg, 0.122 mmol) in acetone (5 mL) was added. Distilled, deionized water was added dropwise until the solution clouded slightly. Slow evaporation at room temperature resulted in the formation of a red-purple microcrystalline solid. The product was collected on a fritted glass funnel, rinsed with water (10 mL) and pentane (10 mL), and dried in vacuo. Yield 18.6 mg (49.9%) of [Tc(NO)(PPh_3)($Spy)_2$].

Anal. Calcd for $C_{28}H_{23}N_3OPS_2Tc$: C, 54.99; H, 3.76; N, 6.87; S, 10.47.

Found: C, 54.88; H, 3.74; N, 6.82; S, 10.55.

FABMS(+) (*m/z*): 611 [Tc(NO)PPh_3($Spy)_2$]$^+$, 581 [TcPPh_3($Spy)_2$]$^+$, 534 [Tc(NO)PPh_3(Spy)SH]$^+$, 501 [Tc(NO)PPh_3(Spy)]$^+$, 349 [Tc(NO)($Spy)_2$]$^+$, 319 [Tc($Spy)_2$]$^+$.

IR (KBr) (cm^{-1}): ν (NO) 1677 (vs).

^1H-NMR ($(CD_3)_2CO$): δ=8.30 (d of d, 1H), 7.56 (m, 7H), 7.37 (m, 10H), 7.11 (t of d, 1H), 6.93 (d of d, 1H), 6.86 (m, 1H), 6.51 (d of d, 1H), 6.22 (t of d, 1H).

^{99}Tc-NMR ($(CD_3)_2CO$): δ= 801 ppm, linewidth 2730 Hz (δ TcO_4^- is 0 ppm).

Results and Discussion

In the reaction of $[Tc(NO)Cl_2(PPh_3)_2(NCCH_3)]$ **[2]** with potassium alkyl xanthate, each bidentate, monoanionic xanthate ligand displaces one chloride and one neutral ligand to yield neutral technetium(I) complexes of the general formula $[Tc(NO)Cl_{2-X}(PPh_3)_{3-X}(S_2COR)_X]$ (X=1, R=isobutyl; X=2, R=neopentyl, isobutyl, methyl). As both derivatives $[Tc(NO)Cl(PPh_3)_2(S_2COR)]$ and $[Tc(NO)(PPh_3)(S_2COR)_2]$ are prepared under the same temperature conditions, the desired product can be controlled based on reaction stoichiometry. Similar selectivity in substitution reactions with xanthate ligands is seen in the formation of $[Tc(CO)_2(PPh_3)_2(S_2COR)]$ from $[Tc(CO)_3(PPh_3)_2Cl]$.[9]

Characterization of the xanthate derivatives by infrared spectroscopy (**Figure IV-2**) indicates that the linear, NO^+ binding mode of the nitrosyl group has not been disturbed as a result of the ligand exchange; the nitrosyl absorbances of both $[Tc(NO)Cl(PPh_3)_2(S_2COR)]$ and $[Tc(NO)(PPh_3)(S_2COR)_2]$ are centered around 1700 cm^{-1}, at the low end of the range established for linear nitrosyl ligands.[21] Bands characteristic of the xanthate ligand are also prominent in the IR spectra of the nitrosyl xanthate complexes. Each derivative displays a single broad band which is located in the range of 1229 - 1244 cm^{-1} and is attributable to the xanthate C=S stretch. This band location indicates the presence of bidentate rather than monodentate xanthate coordination.[22] In addition, bands from the C-O absorbances are clustered near 1047 cm^{-1}, in the range reflecting a partial C-O double bond character and contribution from the ionic resonance structure of the xanthate ligand in these complexes (**Figure IV-1A-II**).[1,22] The steric bulk of the alkyl xanthate ligand does not appear to affect the xanthate coordination mode or the technetium-nitrosyl linkage, as little change is evident in the infrared when the R substituent is changed from the methyl to isobutyl to neopentyl group. Similar results have been obtained in the series of Tc(III) xanthates, $[Tc(PPh_3)(S_2COR)_3]$ (R is ethyl, isopropyl, n-butyl, or neopentyl).[1]

Relatively few ^{99}Tc chemical shifts have been reported for technetium sulfur complexes due to the difficulty in observing these typically broad signals. Complexes containing xanthate[1,8] and dithiocarbamate[8] ligands were the first technetium sulfur compounds for which ^{99}Tc-NMR resonances were identified. The nitrosyl xanthate derivatives presented here also give observable ^{99}Tc-NMR resonances, ranging from 3.5 ppm for $[Tc(NO)Cl(PPh_3)_2(S_2COiBu)]$ to 285 ppm for $[Tc(NO)(PPh_3)(S_2COMe)_2]$. These chemical shfts are located in between the lowfield resonances observed for nitrosyltechnetium complexes of aromatic amines (625 to 2273 ppm) and the highfield signals found for nitrosyl complexes with π-acceptor ligands (-329 to -673 ppm). Xanthate complexes from the series $[Tc(PPh_3)(S_2COR)_3]$ exhibit broad ^{99}Tc resonances near 2860 ppm, with typical linewidths of 7800 Hz.[1] By comparison, the chemical shifts of the xanthate derivatives prepared here appear far upfield, a difference attributable[20] to the change in oxidation state from Tc(III) in the phosphine complexes to Tc(I) in the nitrosyl derivatives; the nitrosyl xanthate resonances more closely resemble that of $[Tc^{I}(CO)(S_2CNR_2)_3]$ at 590 ppm.[8] The fewer number of sulfur atoms present in the technetium coordination spheres of $[Tc(NO)Cl(PPh_3)_2(S_2COR)]$ and $[Tc(NO)(PPh_3)(S_2COR)_2]$ allows more narrow ^{99}Tc signals to be observed in these complexes than was seen for either the trisxanthate[1] or the trisdithiocarbamate[8] derivatives.

$[Tc(NO)Cl(PPh_3)_2(S_2COiBu)]$

The reaction of **[2]** with exactly one equivalent of potassium isobutylxanthate gives the bright yellow complex $[Tc(NO)Cl(PPh_3)_2(S_2COiBu)]$ **[22]** in moderate yield. Characterization of the product by mass spectrometry shows a molecular ion peak at 837 *m/z* and fragmentation peaks resulting from the loss of chloride (802 *m/z*), isobutylxanthate (688 *m/z*), triphenylphosphine (575 *m/z*), and both chloride and triphenylphosphine (540 *m/z*). The IR spectrum of **[22]** exhibits a very strong nitrosyl stretch at 1702 cm^{-1}; a strong, broad C=S band is positioned at 1238 cm^{-1} due to the bidentate xanthate ligand. Analysis of $[Tc(NO)Cl(PPh_3)_2(S_2COiBu)]$ by ^1H-NMR spectroscopy clearly demonstrates that the two triphenylphosphine ligands are equivalent and are coordinated in a *trans* geometric configuration. In addition, the resonances assigned to the xanthate ligand show the splitting pattern and integrations expected for an isobutyl group.

$[Tc(NO)(PPh_3)(S_2COR)_2]$

The bright red-orange complex $[Tc(NO)(PPh_3)(S_2COR)_2]$ is formed in the reaction of $[Tc(NO)Cl_2(PPh_3)_2(NCCH_3)]$ **[2]** with excess potassium xanthate in refluxing dichloromethane. Crystalline samples can be obtained in moderate to good yields by slow evaporation of a layered mixture of acetone, methanol, and water; when crystallized in this manner, the complex contains acetone in the crystal lattice, as determined through elemental analysis and ^1H-NMR spectroscopy. The lipophilicity of the complex can be altered by changing the R substituent at the xanthate terminus, and derivatives containing the neopentyl **[24]**, isobutyl **[25]**, and methyl **[26]** groups were prepared for comparison purposes. The alkyl substituent appears to significantly affect only the isolated yield of the reaction; the steric bulk of the neopentyl derivative aids in complex crystallization, resulting in an 80% product yield versus an observed 44% yield for the methyl analog. Otherwise, few significant differences between derivatives are evident in the characterization of these bisxanthate nitrosyl complexes.

Analysis of $[Tc(NO)(PPh_3)(S_2COR)_2]$ through spectroscopic means is straightforward, as no fluxional behavior is evident in solutions of these bisxanthate complexes. As discussed above, infrared spectroscopy confirms a linear NO^+ group and bidentate xanthate coordination. While two geometric isomers are theoretically possible for this ligand configuration, data from ^{1}H-NMR spectroscopy indicates that the geometry pictured in **Figure IV-3A** is represented in the complex. The ^{1}H-NMR spectrum of each derivative $[Tc(NO)(PPh_3)(S_2COR)_2]$ in CD_2Cl_2 shows two sets of alkyl xanthate resonances resulting from inequivalent xanthate ligands. Of the two possible isomers depicted in **Figure IV-3**, only the asymmetrical geometry of Structure **A** could account for this spectrum.

A detailed analysis of the ^{1}H-NMR spectrum of the isobutylxanthate derivative, $[Tc(NO)(PPh_3)(S_2COiBu)_2]$ **[25]** (**Figure IV-4**), yields additional structural information. Six isobutylxanthate resonances appear in the region of the spectrum from 0.80 to 4.50 ppm. The set of resonances at 1.04, 2.19, and 4.42 ppm represent xanthate ligand **1**, which is coordinated *cis,cis* to the nitrosyl, whereas the peaks at 0.86, 1.86, and 3.88 ppm arise from xanthate ligand **2**, coordinated *cis,trans* to the nitrosyl group (inset, **Figure IV-4**). The first order coupling present in $[Tc(NO)(PPh_3)(S_2COiBu)_2]$ was identified through a two-dimensional homonuclear shift correlation experiment, which confirmed this peak assignment and showed no interactions between the two isobutylxanthate ligands (**Figure IV-5**). The resonances of xanthate ligand **1** appear analogous to those observed for the monoxanthate derivative **[22]**. However, the second set of xanthate resonances is shifted upfield from this standard location due to shielding of the xanthate ligand **2** by the triphenylphosphine rings.[23] The diamagnetic anisotropy of the benzene rings creates an environment in which the methylene hydrogens become diastereotopic and an interesting splitting pattern results. Rather than appearing as a simple doublet like observed for peak **1A**, the methylene hydrogens of xanthate ligand **2** resonate as an 8-line pattern at 3.88 ppm (**2A**). The diastereotopic methylene hydrogens have slightly different chemical shifts and couple, resulting in the formation of a pair of doublets. Each doublet is split again through coupling with the neighboring methine hydrogen, yielding the observed 8-line splitting pattern. When the methine hydrogen (peak **2B**, 1.86 ppm) is decoupled from this spin system, the signal of the methylene hydrogens from xanthate **2** collapses to a pair of doublets, showing the net coupling of the diastereotopic hydrogens (**Figure IV-6B**). In contrast, decoupling of the methine resonance in xanthate ligand **1** (peak **1B**, 2.19 ppm) causes the signal of the magnetically equivalent methylene hydrogens to collapse into a singlet (**Figure IV-6C**). The bisxanthate derivatives **[24]** and **[26]** also exhibit this triphenylphosphine-induced anisotropy in the *cis,trans*-xanthate ligand.

Slight differences are observed in the fragmentation patterns produced by the various xanthate derivatives in the fast atom bombardment mass spectrum. The mass spectral data of the xanthate derivatives $[Tc(NO)(PPh_3)(S_2COR)_2]$ is summarized in **Table IV-1**. Most notable is the presence of peaks from sulfido species generated in the mass spectra of primarily the neopentyl and isobutyl derivatives; sulfido formation from xanthate complexes has been noted previously.[1]

The chemical shifts of the nitrosyl bisxanthate complexes as determined by ^{99}Tc-NMR spectroscopy are listed in **Table IV-2**. Two trends become evident as the steric bulk of the alkyl substituent is increased. Larger R groups result in greater shielding of the technetium nucleus and hence a slight shift of the technetium resonance to higher field, lower ppm values.[20] In addition, a corresponding broadening of the signal is observed as the steric bulk increases and the symmetry of the complex is lowered. In contrast, the nitrosyl stretching vibrations of the bisxanthate derivatives appear almost identical by infrared spectroscopy, despite the variation in alkyl substituents. These observations highlight the enhanced sensitivity of ^{99}Tc-NMR spectroscopy as a means of detecting slight changes in the electronic environment of the metal center.

Reactions of [Tc(NO)Cl_2(PPh_3)$_2$($NCCH_3$)] with 2-mercaptopyridine

Complexes analogous to the xanthate derivatives discussed above can be synthesized from [Tc(NO)Cl_2(PPh_3)$_2$($NCCH_3$)] **[2]** and 2-mercaptopyridine. The presence of the proton sponge 1,1,3,3-tetramethylguanidine in the reaction mixture ensures deprotonation of 2-mercaptopyridine and subsequent coordination as the bidentate, monoanionic ligand rather than as the neutral species.

When complex **[2]** and the ligand are combined in refluxing dichloromethane, the acetonitrile and one chloride ion are exchanged and the lilac-purple complex [Tc(NO)Cl(PPh_3)$_2$(Spy)] **[23]** is formed. A linear NO^+ group is evident from the very strong, broad absorbance at 1696 cm^{-1} in the IR spectrum of the complex. As with the monoxanthate complex **[22]**, a *trans*-triphenylphosphine ligand geometry is indicated by ^{1}H-NMR spectroscopy; resonances from the four aromatic hydrogens of the 2-mercaptopyridine ligand are also clearly visible.

Higher temperature conditions result in the formation of the red-purple complex [Tc(NO)(PPh_3)(Spy)$_2$] **[27]** rather than **[23]**. A geometry analogous to that of the bisxanthate derivatives [Tc(NO)(PPh_3)(S_2COR)$_2$] is indicated for **[27]**, as inequivalent 2-mercaptopyridine ligands are shown by ^{1}H-NMR spectroscopy. The complex gives a molecular ion peak at 611 *m/z* in the mass spectrum and a predictable fragmentation profile. In addition to the loss of the nitrosyl, triphenylphosphine, and 2-mercaptopyridine groups, fragments corresponding to sulfido species are generated and can be observed in the mass spectrum, similar to the mass spectral behavior of the xanthate complexes $[Tc(NO)(PPh_3)(S_2COR)_2]$ and $[Tc(PPh_3)(S_2COR)_3]$.[1] A lower frequency nitrosyl stretching vibration is evident in the infrared spectrum of **[27]** than was seen for the bisxanthate nitrosyl derivatives; the presence of pyridine-based ligands in $[Tc(NO)(PPh_3)(Spy)_2]$ and the subsequent increase in metal-to-nitrosyl back-donation causes this very low 1677 cm^{-1} absorbance.

The presence of pyridine-nitrogens in the technetium coordination sphere also contributes to the downfield shift observed in the ^{99}Tc-NMR resonances of $[Tc(NO)Cl(PPh_3)_2(Spy)]$ and $[Tc(NO)(PPh_3)(Spy)_2]$ relative to their xanthate counterparts. Chemical shifts of 657 and 801 ppm, respectively, are observed for the 2-mercaptopyridine complexes. Thus, data from ^{99}Tc-NMR spectroscopy confirms that the electronic environment of the technetium in each 2-mercapto-pyridine derivative is intermediate between that of the analogous nitrosyltechnetium complex with all sulfur or with all nitrogen ligation.

Summary

Exchange of the chloride ligands in $[Tc(NO)Cl_2(PPh_3)_2(NCCH_3)]$ can be achieved through reactions with the monoanionic, bidentate ligands isobutyl-xanthate and 2-mercaptopyridine. Variations in the reaction conditions allow the formation of $[Tc(NO)Cl(PPh_3)_2(S_2COiBu)]$ **[22]**, $[Tc(NO)Cl(PPh_3)_2(Spy)]$ **[23]**, $[Tc(NO)(PPh_3)(S_2COiBu)_2]$ **[25]**, and $[Tc(NO)(PPh_3)(Spy)_2]$ **[27]**. The alkyl substituent at the xanthate terminus can be altered without significantly affecting the spectroscopic properties of the complex or the technetium-nitrosyl linkage.

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Table IV-1. Observed Mass Spectral Results for [$Tc(NO)(PPh_3)(S_2COR)_2$] Derivatives.

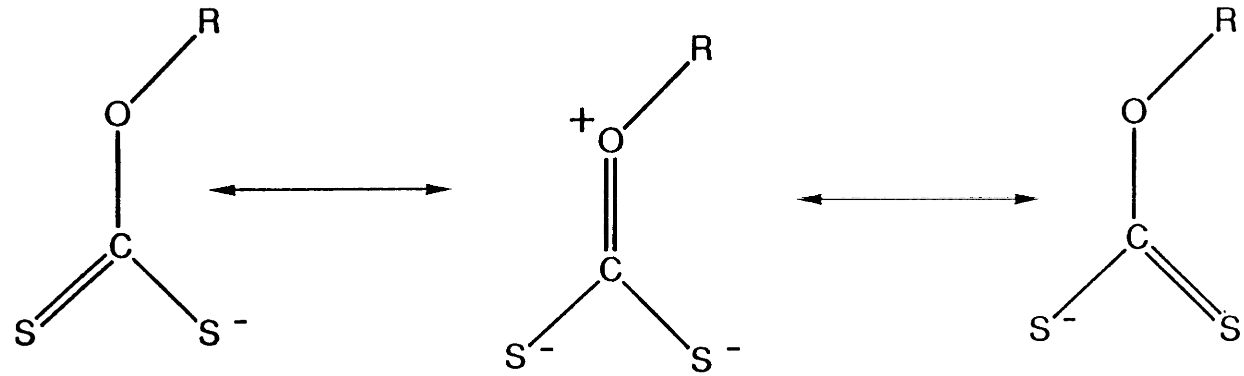
Species[1]	Xanthate Derivative	Mass, *m/z*
$Tc(NO)PL_2^+$	neopentyl	717
	isobutyl	689
	methyl	605
$Tc(NO)PLSH^+$	neopentyl	587
	isobutyl	573
	methyl	531
$Tc(NO)PL^+$	neopentyl	554
	isobutyl	540
	methyl	499
$Tc(NO)L_2^+$	neopentyl	456
	isobutyl	----[2]
	methyl	342
$Tc(NO)PS^+$	neopentyl	423
	isobutyl	423
	methyl	----

1. $P=PPh_3$, $L=S_2COR$.
2. ---- indicates that no significant peak was observed for these species.

Table IV-2. ^{99}Tc-NMR Data for $[Tc(NO)(PPh_3)(S_2COR)_2]$ Derivatives.

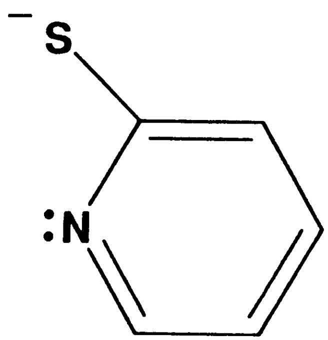
Xanthate Derivative	Chem. Shift, ppm	Linewidth, Hz
neopentyl	271	2850
isobutyl	278	2605
methyl	285	2230

Figure IV-1. Structures of the sulfur ligands used in this study.



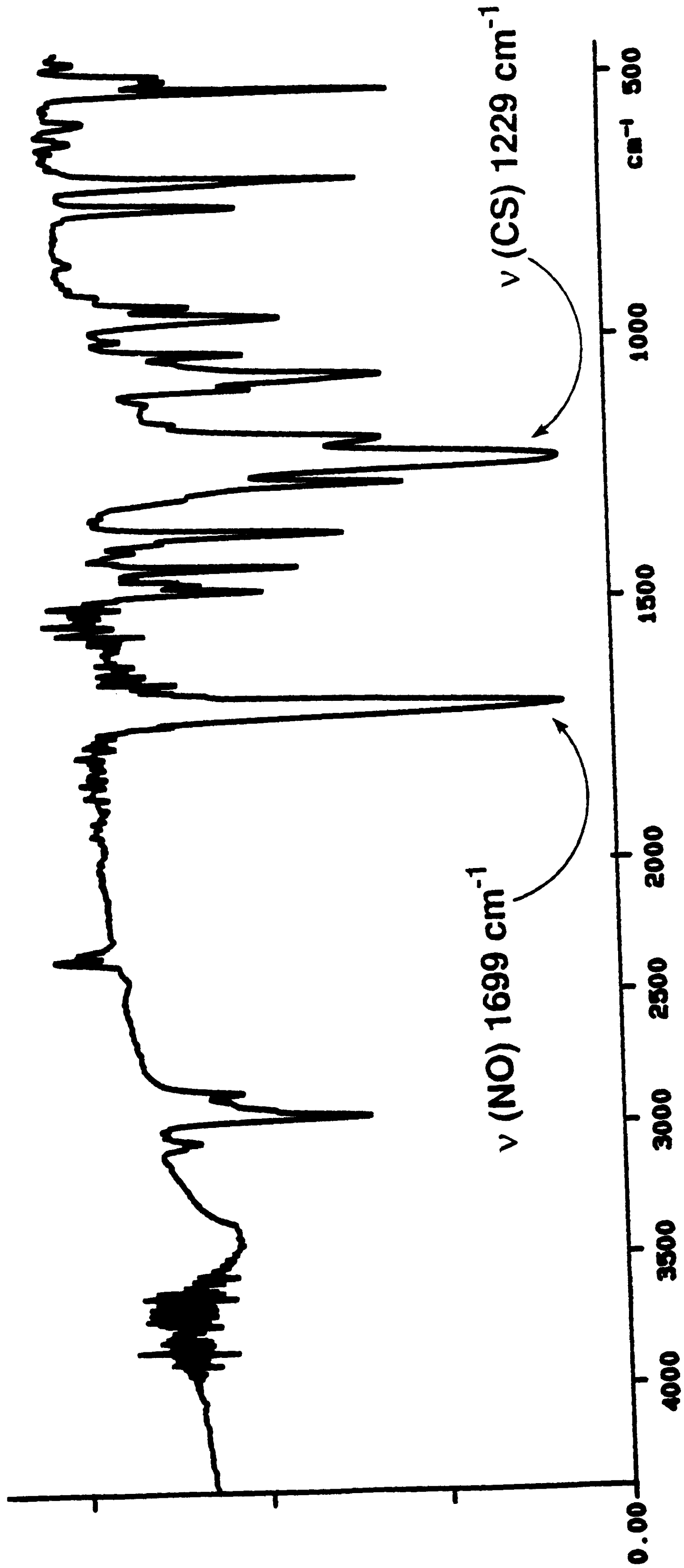
A - I **A - II** **A - III**

R = methyl, isobutyl, or neopentyl group



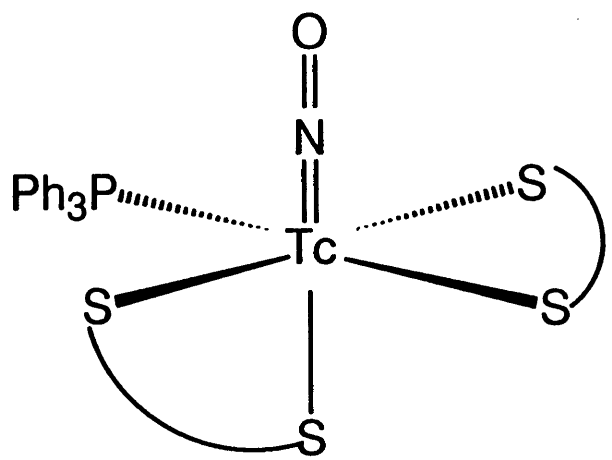
B

Figure IV-2. Infrared spectrum of $[Tc(NO)(PPh_3)(S_2COnPe)_2]$ **[24]**, obtained in KBr.

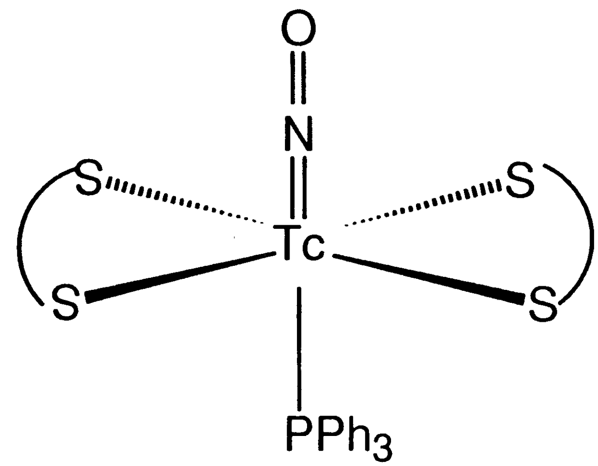


ν (NO) 1699 cm^{-1}
ν (CS) 1229 cm^{-1}
4000
3500
3000
2500
2000
1500
1000
500
cm^{-1}
0.00

Figure IV-3. Structures of the possible geometric isomers of $[Tc(NO)(PPh_3)(S_2COiBu)_2]$ **[25]**.

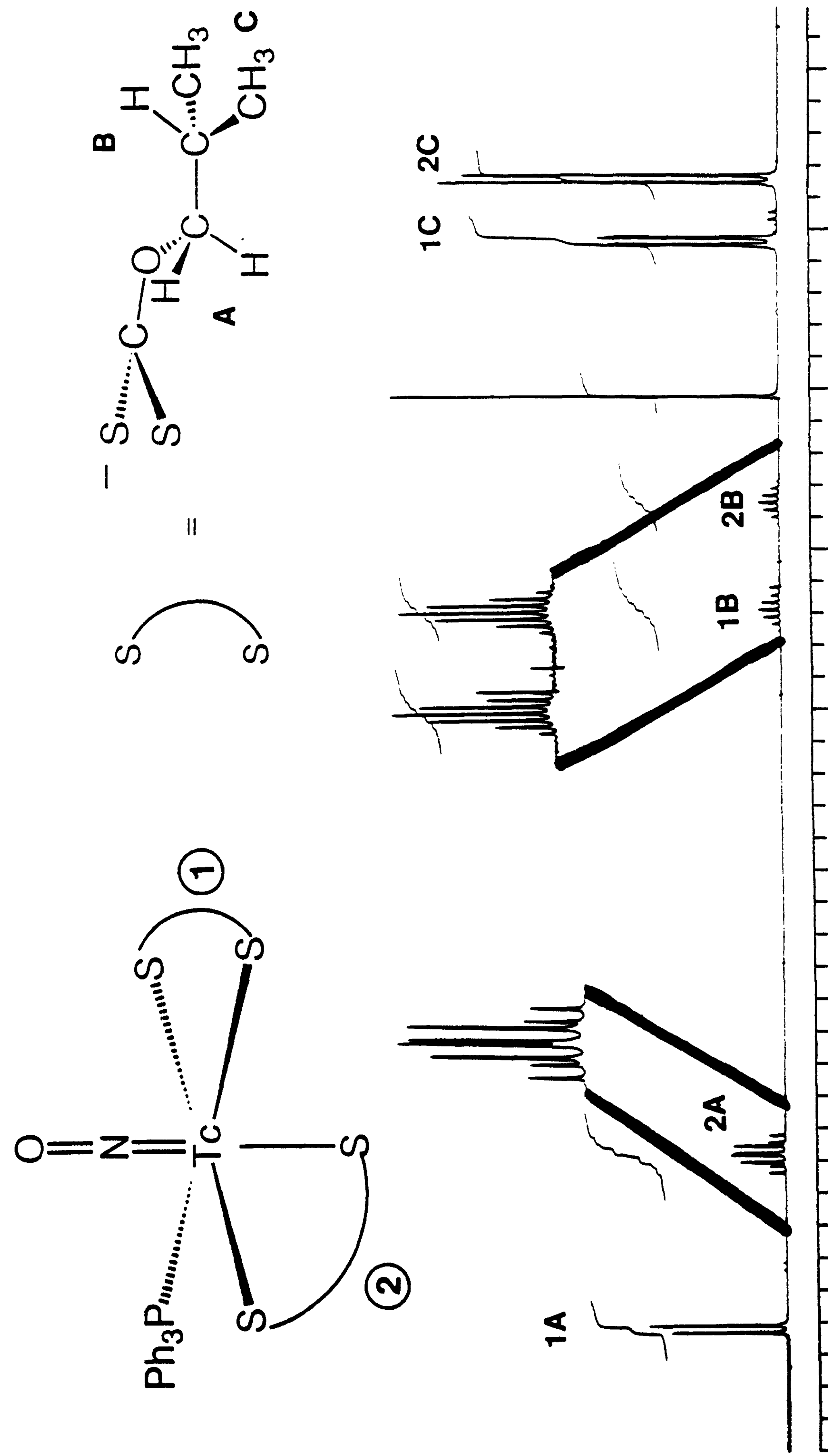


Isomer A



Isomer B

Figure IV-4. A portion of the ^{1}H-NMR spectrum of [Tc(NO)(PPh_3)(S_2COiBu)$_2$] **[25]**, taken in CD_2Cl_2, showing the isobutylxanthate peak assignment and ligand numbering scheme (inset).



Ph3P
Tc
N
O
S
1
2
1A
2A
1B
2B
1C
2C
A
B
C
H
CH3
4.0
3.0
2.0
1.0 PPM

Figure IV-5. ^{1}H-COSY spectrum of [$Tc(NO)(PPh_3)(S_2COiBu)_2$] **[25]**, taken in CD_2Cl_2, showing all first order xanthate coupling in the region from 0.50 to 5.00 ppm.

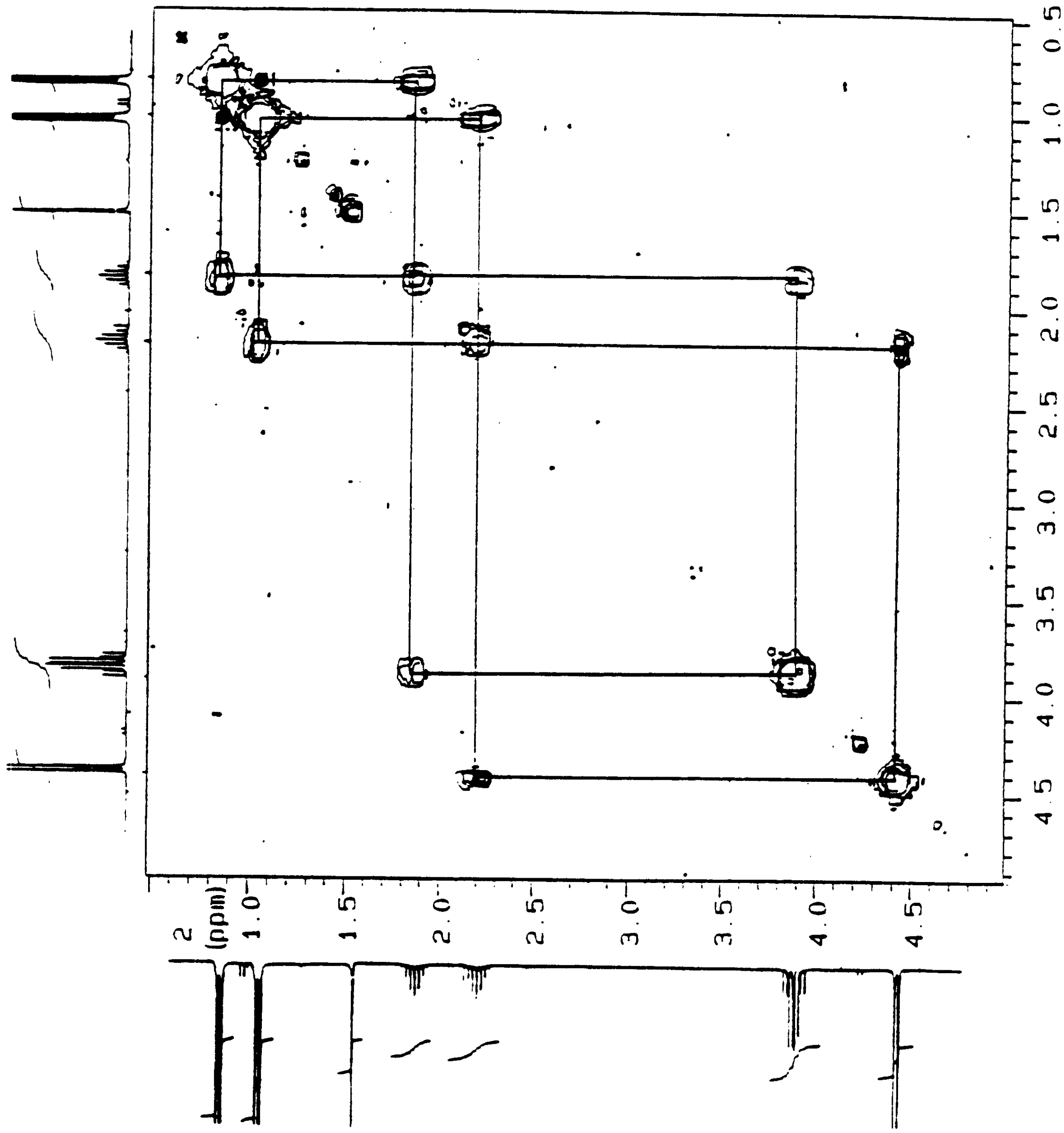
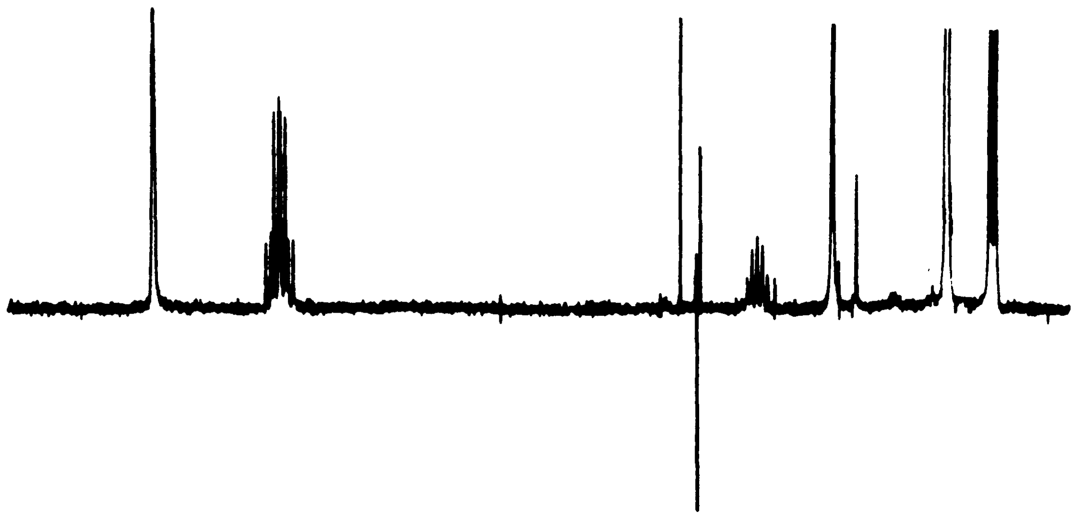
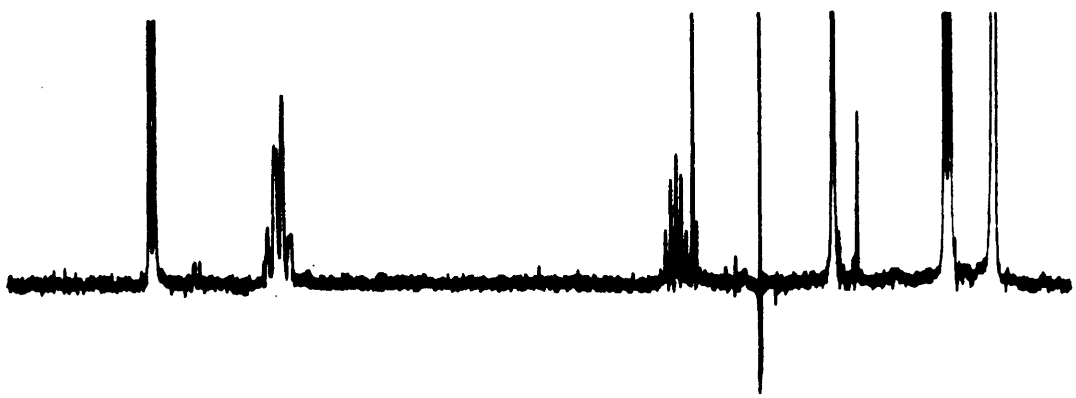

F1 (ppm)
(ppm)

Figure IV-6. Comparison of the ^{1}H-NMR spectrum of $[Tc(NO)(PPh_3)(S_2COiBu)_2]$ **[25]** (**A**) with the spectra obtained after decoupling of the methine hydrogens of the *cis,trans*-xanthate (**B**) and *cis,cis*-xanthate (**C**) ligands.

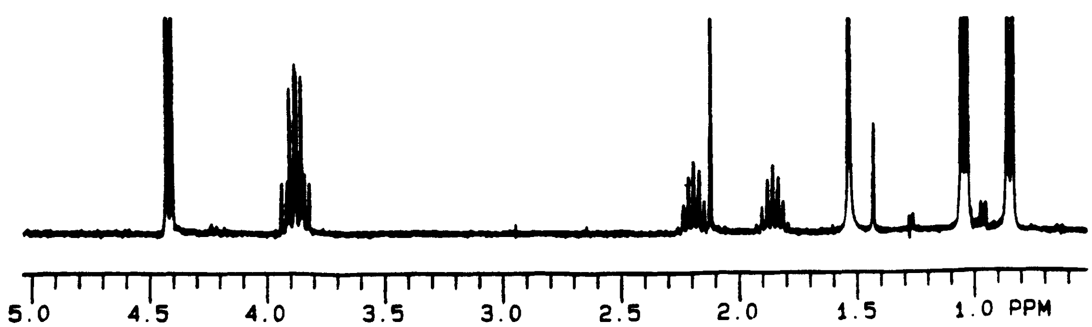
C. Spectrum with *cis,cis*-xan <u>CH</u> decoupled



B. Spectrum with *cis,trans*-xan <u>CH</u> decoupled



A. ^{1}H-NMR of $[Tc(NO)(PPh_3)(xan)_2]$



APPENDIX 1

The Characterization of Technetium(I) Nitrosyl Complexes Using ^{99}Tc-NMR Spectroscopy

Introduction

The favorable properties of the ^{99}Tc nucleus, which include a very high receptivity of 0.275 relative to ^{1}H (**Figure A-1**), have allowed the use of ^{99}Tc-NMR spectroscopy in the characterization of technetium complexes.[1,2] While a number of technetium(I) carbonyl[3-6] and isonitrile[1,2] complexes have been studied by this method, the work presented here is the first reported ^{99}Tc-NMR data for technetium(I) nitrosyl complexes. The NO^+ moiety causes the observed ^{99}Tc-NO signals to be shifted downfield from those of the Tc(I) complexes with similar π-acid ligands. The various effects of the NO^+, aromatic amines, π-acceptors, and thiolate ligands on the electronic environment of the technetium nucleus are discussed herein relative to the known trends[1] in ^{99}Tc-NMR spectroscopy.

Experimental Section

Caution: Technetium-99 is a weak β^- emitter (E=292 keV, $t_{1/2}$= 2.12 x 10^5 years). All manipulations of solutions and solids were performed in laboratories approved for the use of low-level radioactivity, following precautions detailed elsewhere.[7]

All of the nitrosyltechnetium(I) complexes were prepared as described in Chapters 1 - 4 of this work except $[Tc(NO)(CNtBu)_5](PF_6)_2$, which was synthesized according to the literature method.[8]

The ^{99}Tc NMR spectra were recorded at room temperature using a Varian XL-300 MHz spectrometer, following the procedures outlined in Chapters 1 - 4. All spectra were obtained using CD_2Cl_2 as solvent, unless otherwise indicated.

Results and Discussion

The ^{99}Tc chemical shifts of the series of technetium(I) nitrosyl complexes presented in this investigation are summarized in **Tables A-1** through **A-3**. The linewidths of these ^{99}Tc signals are rather broad, ranging in size from 1860 to 8680 Hz. Such broad signals are typically obtained from molecules of the quadrupolar technetium nucleus which possess lower symmetry.[1] No coupling between the ^{99}Tc and ^{31}P nuclei could be differentiated in these broad resonances.

Several trends in the ^{99}Tc signal location and appearance have been noted in the study of technetium complexes by ^{99}Tc-NMR spectroscopy. A correlation between the technetium oxidation state and observed chemical shift was noted.[1] The "Tc(I) window" was reported as -1460 to -3517 ppm, with windows located farther downfield for higher oxidation states of the metal. The nitrosyltechnetium(I) signals presented here do not fall within the prescribed Tc(I) range established with ^{99}Tc-NMR data from Tc(I) carbonyl and isonitrile complexes. Rather, the resonances occur downfield, within the Tc(III) and Tc(V) windows.[1] This significant downfield shift results from greater deshielding[9] of the technetium nucleus by the NO^+ moiety. Substitution of the cationic NO^+ group for the neutral carbonyl or isonitrile ligands reduces the electron density at the technetium nucleus and results in greater deshielding and the observed downfield shift. As more diamagnetic technetium(I) complexes are synthesized and characterized, it is likely that the accepted technetium(I) oxidation state window will broaden significantly and make the past correlations between technetium chemical shift and oxidation state ambiguous. The recent report[10] of a ^{99}Tc chemical shift of 645 ppm for the thionitrosyl complex *mer*-[$Tc(NS)Cl_2(Me_2PhP)_3$] lends credence to this prediction.

As depicted in **Figure A-2**, the ^{99}Tc-NMR signals of the new nitrosyl complexes are found to range from -673 ppm to 2273 ppm relative to the pertechnetate ion standard and correlate with the ligand environment of the technetium nucleus. The signals located farthest upfield, from -329 to -673 ppm, arise from the nitrosyl complexes with π-accepting ligands, whereas those farthest downfield, from 625 to 2273 ppm, correspond to the nitrosyl complexes containing aromatic amines; nitrosyl complexes with sulfur ligation are found at an intermediate location, from 3.5 to 801 ppm. This increase in observed chemical shift upon substitution of aromatic amines for π-acceptors arises from the relative decrease in ligand field strength; the larger chemical shift values are associated with greater deshielding of the ^{99}Tc nucleus and a smaller HOMO-LUMO gap.[9,11] This trend is demonstrated in the series of 3,5-lutidine (lut) complexes [$Tc(NO)Cl_2(PPh_3)_2(lut)$], [$Tc(NO)Cl_2(PPh_3)(lut)_2$], and [$Tc(NO)Cl_2(lut)_3$]. As additional moderate field lutidine ligands are placed on the technetium metal center, the ^{99}Tc chemical shift increases from 940 to 1382 to 2197 ppm, respectively. Conversely, sequential addition of the strong field π-acid ligand *tert*-butylisonitrile (CNtBu) to the technetium nitrosyl core in the series [$Tc(NO)Cl_2(PPh_3)_2(CNtBu)$], [$Tc(NO)Cl_2(PPh_3)(CNtBu)_2$], and [$Tc(NO)Cl_2(CNtBu)_3$] results in a shift of the ^{99}Tc signals to higher field, corresponding to an increase in shielding and in the size of the HOMO-LUMO gap. This trend is shown pictorially in **Figure A-3**. By comparison, the ^{99}Tc-NMR signal of the pentakisisonitrile complex[8] [$Tc(NO)(CNtBu)_5$](PF_6)$_2$ is located even farther upfield at -1320 ppm.

Thus, like the spectrochemical series of optical spectroscopy, the technique of ^{99}Tc-NMR spectroscopy gives a direct measurement of the effect of a specific ligand environment on the electronic properties of the metal. In addition, the ^{99}Tc signals can be used to differentiate between technetium(I) complexes containing nitrosyl, carbonyl, and isonitrile ligands.

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12. Taken from O'Connell, L. A. Ph.D. Thesis, Massachusetts Institute of Technology, September 1989.

Table A-1. The ^{99}Tc-NMR Chemical Shifts and Linewidths for Tc(I) Nitrosyl Complexes with Nitrogen Ligation.

Compound	δ, ppm	Linewidth, Hz
$Tc(NO)Cl_2(PPh_3)_2(NCCH_3)$	623	4700
$Tc(NO)Br_2(PPh_3)_2(NCCH_3)$	582	5460
$Tc(NO)Cl_2(PPh_3)_2(py)$	625, 950	5000
$Tc(NO)Cl_2(PPh_3)_2(lut)$	940	4715
$Tc(NO)Cl_2(PPh_3)(py)_2$	1379	3000
$Tc(NO)Cl_2(PPh_3)(lut)_2$	1382	3600
$Tc(NO)Cl_2(PPh_3)(phen)$	1477	4960
$Tc(NO)Cl_2(py)_3$	2160	1860
$Tc(NO)Cl_2(lut)_3$	2197	2730
$Tc(NO)Cl_2(terpy)$*	2273	3970

*Due to low solubility in CD_2Cl_2, this spectrum was obtained in DMF-d_7.

Table A-2. The ^{99}Tc-NMR Chemical Shifts and Linewidths for Tc(I) Nitrosyl Complexes containing π-Acceptor Ligands.

Compound	δ, ppm	Linewidth, Hz
$Tc(NO)Cl_2(PPh_3)_2(CNR)^{A,B}$	-329	4090
$Tc(NO)Cl_2(PPh_3)(CNR)_2$	-380	4700
$Tc(NO)Cl_2(CNR)_3$	-498	5700
$Tc(NO)Br_2(CNR)_3$	-596	6950
$Tc(NO)Cl_2(PPh_3)_2(CO)$	-618	2480
$Tc(NO)Br_2(PPh_3)_2(CO)$	-673	2850
$[Tc(NO)(CNR)_5](PF_6)_2$	-1320	744

A. R is the *tert*-butyl group.

B. This spectrum was obtained in 3:1 C_6D_6/CD_2Cl_2.

Table A-3. The ^{99}Tc-NMR Chemical Shifts and Linewidths for Tc(I) Nitrosyl Complexes containing Sulfur Ligation.

Compound	δ, ppm	Linewidth, Hz
$Tc(NO)Cl(PPh_3)_2(S_2COR)^A$	3.5	2230
$Tc(NO)(PPh_3)(S_2COR)_2$	278	2605
$Tc(NO)Cl(PPh_3)_2(Spy)^B$	657	8680
$Tc(NO)(PPh_3)(Spy)_2$	801	2730

A. R is the isobutyl group.

B. The spectra of the 2-mercaptopyridine complexes were obtained in acetone-d_6.

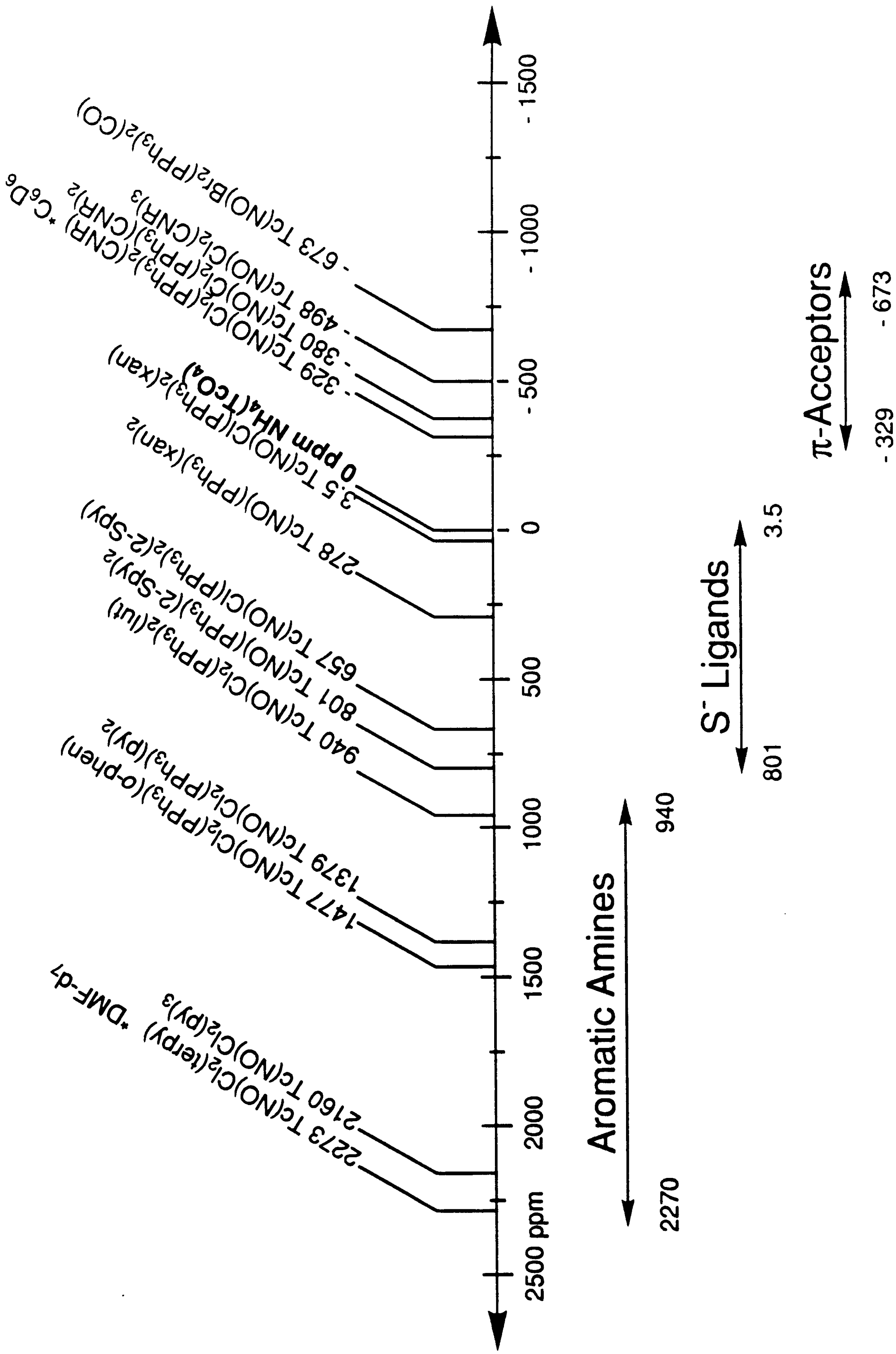
Figure A-1. Properties of the ^{99}Tc nucleus.[12]

Properties of the ^{99}Tc Nucleus

spin, I	9/2
natural abundance, a	100 %
magnetogyric ratio, g	6.0211×10^{7} rad. T^{-1} s^{-1}
quadrupole moment, Q	0.3×10^{-28} m^{2}
sensitivity, s (relative to ^{1}H = 1.000)	0.375
receptivity, R/ ^{13}C	2,134
Fifth most sensitive nucleus	
T_1, typical values	2×10^{-1} s and below

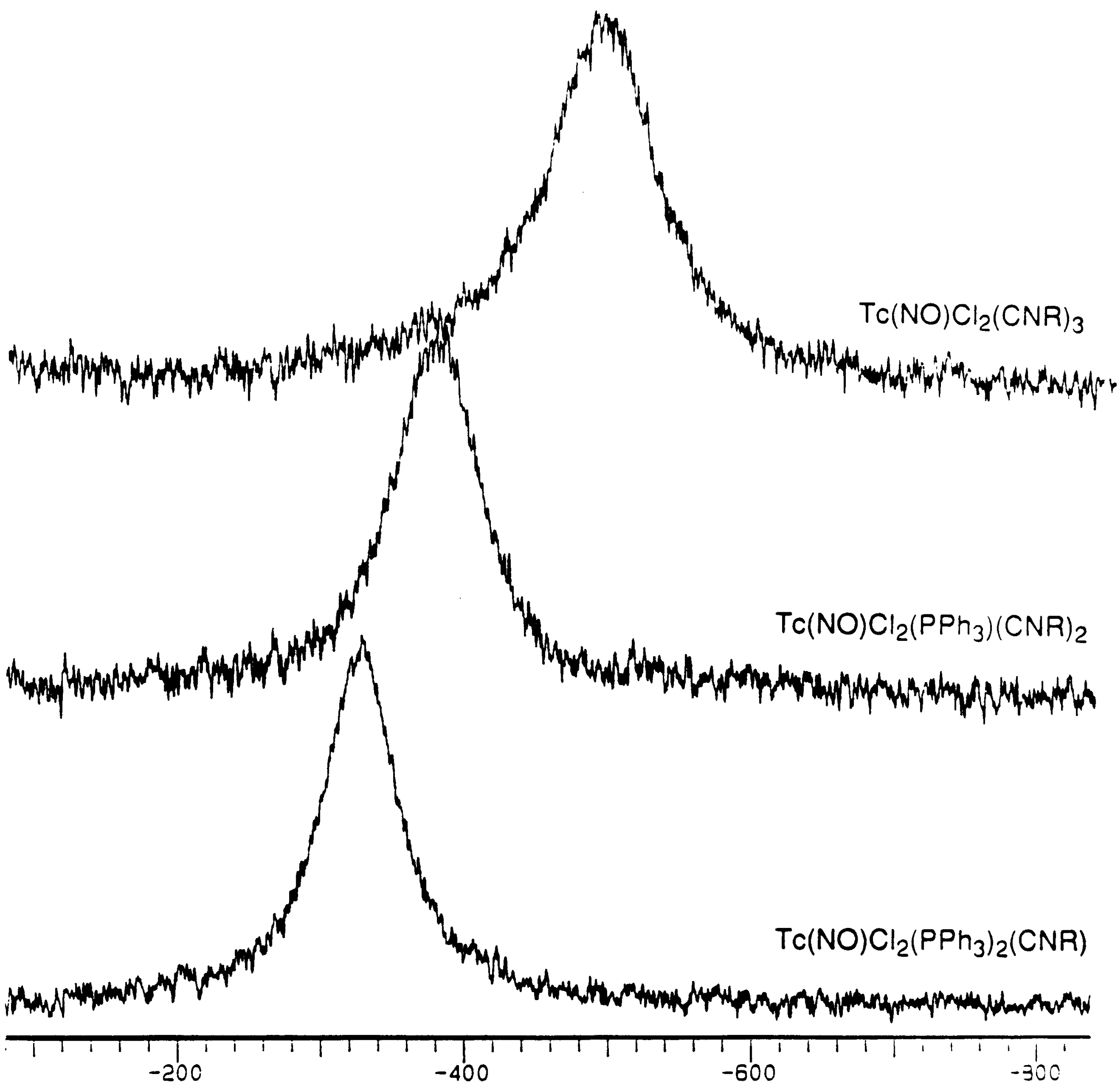
Resonance frequency of TcO_4^- on 300 MHz spectrometer 67.516 MHz

Figure A-2. Observed ^{99}Tc chemical shift ranges of the Tc-nitrosyl complexes, divided according to ligand environment.



2500 ppm
2000
1500
1000
500
0
- 500
- 1000
- 1500
2273 Tc(NO)Cl$_2$(terpy) *DMF-d$_7$
2160 Tc(NO)Cl$_2$(py)$_3$
1477 Tc(NO)Cl$_2$(PPh$_3$)(o-phen)
1379 Tc(NO)Cl$_2$(PPh$_3$)(py)$_2$
940 Tc(NO)Cl$_2$(PPh$_3$)$_2$(lut)
801 Tc(NO)(PPh$_3$)(2-Spy)$_2$
657 Tc(NO)Cl(PPh$_3$)$_2$(2-Spy)
278 Tc(NO)(PPh$_3$)(xan)$_2$
3.5 Tc(NO)Cl(PPh$_3$)$_2$(xan)
0 ppm NH$_4$(TcO$_4$)
- 329 Tc(NO)Cl$_2$(PPh$_3$)$_2$(CNR) *C$_6$D$_6$
- 380 Tc(NO)Cl$_2$(PPh$_3$)(CNR)$_2$
- 498 Tc(NO)Cl$_2$(CNR)$_3$
- 673 Tc(NO)Br$_2$(PPh$_3$)$_2$(CO)
Aromatic Amines
2270
940
S$^-$ Ligands
801
3.5
π-Acceptors
- 329
- 673

Figure A-3. ^{99}Tc-NMR spectra of a series of Tc-NO isonitrile complexes, obtained in CD_2Cl_2 except where noted.



All spectra were recorded at 67.490 MHz. in CD_2Cl_2.
[$Tc(NO)Cl_2(PPh_3)_2(CNR)$] was dissolved in 3 C_6D_6:1 CD_2Cl_2
in order to slow sample decomposition.

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As it is true that "I am a part of all that I have met", I owe thanks to many wonderful people for their help and encouragement during my work at M.I.T. I thank my advisor, Dr. Alan Davison, for his faith in me and for allowing me to work independently and to make my own choices. I also extend my appreciation to Dr. Alun Jones for his support. I am grateful to my chemistry mentors, Sister Martha Belke, Father James Lambert, and Dr. Barry Corona, for providing both the inspiration and the tools needed to study chemistry at M.I.T.

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My research was made an easier task by the efforts of many excellent chemistry department personnel. The Spec Lab staff, Scott Gardner, Jeanne Owens, Jim Simms, and Debbie Western, were all very helpful in teaching me how to use the instruments or perform special NMR experiments. I thank Dr. Bill Davis for his efforts in solving my many disordered nitrosyl crystal structures. I am also indebted to Chen-hui Zeng and Dr. Catherine Costello for the clues provided in the analysis of my complexes by mass spectrometry. Melinda Glidden Cerny, Launa Abdullah, and Marilyn Mason were always willing to lend much appreciated support. I also wish to thank Dr. Michael Clarke of Boston College for his assistance with the magnetic susceptibility measurements and the chemistry faculty at St. Anselm College for their enthusiastic support of my research endeavors.

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Most importantly, I thank Dan for always being there and for keeping me true to myself. You are my hero.

Biographical Note

The author was born Shannon Lowry Storm on March 1, 1969 in Westminister, Maryland. Her father's U. S. Air Force career took her to Illinois, Maryland, Germany, New Mexico, and finally Alabama, where she was graduated salutatorian from Montgomery Catholic High School in May 1985. She then moved down to Mobile, Alabama in order to attend Spring Hill College. After graduating magna cum laude with a B. S. in Chemistry in May of 1989, the author chose to challenge herself by entering graduate school in chemistry at M.I.T., where she joined the group of Professor Alan Davison and met her future husband and fellow chemist, Dan Blanchard. Currently, the Blanchards are teaching chemistry in the Benedictine tradition at St. Anselm College in Manchester, New Hampshire.