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SYNTHESIS AND CHARACTERIZATION OF TECHNETIUM AND RHENIUM ORGANOHYDRAZIDE COMPLEXES

by

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by

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ABSTRACT

Chapter 1. Group 7 organohydrazide complexes can be classified into eight monohapto structural types on the basis of X-ray structural data. Classification on this basis provides a way for uniform identification of the ligand structural types present in a complex and for uniform assignment of oxidation states of the metal.

Chapter 2. The organohydrazide chelate complexes, M(III)(NNpy)$(PPh_3)_2Cl_2$ **(1)**, **(3)** (M = Re, Tc), have been synthesized using the organohydrazine, 2-hydrazinopyridine. The chelated organohydrazide is a diazenido(1-) ligand that forms a five-membered ring with the metal center. An X-ray structural analysis of **(1)** indicates that there is a delocalized π-system formed by the chelate ring. These octahedral, d^4 metal complexes have diamagnetic ^1H NMR spectra. Complex **(1)**, $C_{41.50}H_{34}Cl_2N_3O_{0.5}P_2Re$, crystallizes in the triclinic space group $P\bar{1}$ with a = 10.5549(7) Å, b = 12.2699(8) Å, c = 16.8206(12) Å, α = 105.9050(10)°, β = 95.8930(10)°, γ = 111.0100(10)°, V = 1906.1(2)$Å^3$, Z = 2, and R = 0.0650 based on 5268 unique reflections. The FABMS+{*p*-nitrobenzylalcohol} of **(3)** reveals a parent ion peak at 799.2 m/z. The complex $[Re(HNNpy)(NNpy)(PMe_2Ph)_2Cl]^+[Cl]^-$ **(2)** contains a chelated, neutral organodiazene ligand and a linear, diazenido(1-) ligand. The X-ray structural analysis of **(2)**, $C_{26}H_{30}Cl_2N_6P_2Re$, indicates a delocalized π-system formed by the chelate ring. The ^1H NMR spectrum of **(2)** is not paramagnetically shifted. Complex **(2)** crystallizes in the orthorhombic space group $Pna2_1$ with a = 17.383(4) Å, b = 13.967(3) Å, c = 12.002(2) Å, V = 2913.9(10) $Å^3$, Z = 4, and R = 0.0384 based on 3083 unique reflections. Complex **(4)**, $[Tc(HNNpy)(NNpy)(PPh_3)Cl]^+[Cl]^-$, also contains a monodentate, linear diazenido(1-) ligand and a chelated neutral organodiazene ligand. The ^1H NMR spectrum of **(4)** is not paramagnetically shifted.

Chapter 3. Organohydrazide chelate complexes of rhenium and technium have been synthesized using 2-hydrazino-4(trifluoromethyl)pyrimidine. The complexes all contain a chelating organohydrazide that forms a five-member ring with the metal center. The chelate ring forms a delocalized π-system and contributes to the unique electronic characteristics of the d^4, octahedral complexes **(1)**, **(2)** and **(3)**, which all have ^1H NMR spectra characteristic of diamagnetic complexes. An X-ray structural analysis of **(1)**, $Tc(III)(NNC_4H_2N_2CF_3)(PPh_3)_2Cl_2$, was obtained. Complex **(1)**, $C_{41}H_{32}Cl_2F_3N_4P_2Tc$, crystallizes in the triclinic space group $P\bar{1}$ with $a = 11.9193(3)$ Å, $b = 12.7026(3)$ Å, $c = 14.1335(3)$ Å, $\alpha = 109.9320(10)°$, $\beta = 94.1250(10)°$, $\gamma = 105.0490(10)°$, $V = 1912.14(8)$ Å^3, $Z = 2$ and $R = 0.0737$ based on 3528 unique reflections. The complex $Re(III)(NNC_4H_2N_2CF_3)(PPh_3)_2Cl_2$ **(2)** was prepared and characterized. Both **(1)** and **(2)** contain a uninegative, chelating diazenido ligand. An X-ray structural analysis of **(3)**, $Re(III)(NNC_4H_2N_2CF_3)(HNNC_4H_2N_2CF_3)(PPh_3)Cl_2$ was obtained. Complex **(3)**, $C_{28}H_{20}Cl_2F_6N_8PRe$, crystallizes in the monoclinic space group $P2_1/c$ with $a = 10.1292(2)$ Å, $b = 14.92310(10)$ Å, $c = 20.6924(4)$ Å, $\alpha = \gamma = 90°$, $\beta = 92.4560(10)°$, $V = 312497(9)$ Å^3, $Z = 4$ and $R = 0.0807$ based on 4472 unique reflections. Complex **(3)** contains a monodentate, uninegative diazenido ligand and a chelating, α-nitrogen protonated, neutral diazene ligand. A Tc(I) complex **(4)**, $Tc(NO)(NNC_4H_2N_2CF_3)(PPh_3)_2Cl$, was prepared and characterized. Complex **(4)** contains a uninegative, chelating diazenido ligand.

Chapter 4. Rhenium(I) chelated *cis*-amide complexes have been synthesized from $Re(CO)_3(PPh_3)_2Cl$. These complexes are of the form $Re(CO)_2(PPh_3)_2(N\text{-}C(=O)\text{-}R)$ and contain a five-membered chelate ring. Complex **(1)**, $C_{44}H_{40}NO_3P_2Re$, crystallizes in the triclinic space group $P\bar{1}$ with $a = 12.102(2)$ Å, $b = 13.981(2)$ Å, $c = 14.011(2)$ Å, $\alpha = 97.57(3)°$, $\beta = 112.51(3)°$, $\gamma = 94.71(3)°$, $V = 2148(2)$ Å^3, $Z = 2$, $R = 0.067$, and $R_w = 0.073$.

Chapter 5. Reactions using 2-hydrazinoimidizoline and perrhenate and pertechnetate in the presence of triphenylphosphine were conducted. The organohydrazide complex formed is paramagentic possibly due to the fact that the imidizoline ring is not aromatic. The technetium product decomposes to $Tc(N)(PPh_3)_2Cl_2$ in the solid state in a period of days. In addition, 2-hydrazinoimidizoline was reacted with $Tc(NO)(NCMe)(PPh_3)_2Cl_2$.

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CHAPTER 1

Group 7 Organohydrazide Chemistry: Classification of Ligand Type Based on X-ray Structural Data

Introduction

Transition metal organohydrazide complexes, which are defined as complexes containing a metal-nitrogen-nitrogen linkage, have received considerable attention as potential model systems for intermediates in biological nitrogen fixation. In the past, a variety of conventions have been used to describe the nature of the bonding of these ligands in metal complexes. In fact, some of the established conventions are contrary to the bond lengths and angles found in the X-ray structural determinations of these complexes. This chapter proposes the use of X-ray structural data to define the structural types and bonding modes of these ligands. The scope of this chapter is limited to Group 7 mononuclear organohydrazide complexes. The convention that is adopted here assumes all electrons involved in the metal-nitrogen bonds have been donated by the highly reducing hydrazine precursor, accurately reflecting the chemistry observed. In cases where the diazo ligand is generated from the diazonium salt, this convention cannot necessarily be assumed because the reaction conditions have changed from reducing to oxidizing. The eight monohapto structural types of organohydrazide ligands are shown in Figure 1. The structural types are the uninegative, linear, four electron donor diazenido A; the uninegative, bent, two electron donor diazenido B; the neutral, bent, two electron donor diazene Γ; the zwitterionic, neutral, bent, four electron donor isodiazene Δ; the neutral, bent, two electron donor E; the uninegative, bent, two electron donor Z; the unipositive, bent, two electron donor H; and the neutral, bent, two electron donor, hydrazino Θ. Not all of the structural types listed have been observed in Group 7 metal complexes as of yet. It should be noted that within the eight structural types are the possibilities of *cis*- and *trans*-isomers.

Discussion

The diazenido ligand has two forms, the uninegative four electron donor A and the uninegative two electron donor B. Complexes containing structural type A typically have metal-nitrogen bond lengths of 1.7 to 1.8 Å, indicative of multiple bonding, and nitrogen-nitrogen multiple bonding, which is evidenced by the bond lengths of 1.2 to 1.3 Å. The metal-nitrogen-nitrogen bond angle in this structural type is relatively linear. The chelating diazenido ligand form is an interesting case because it has characteristics of A, as seen in the metal-nitrogen bond length, and characteristics of B, as seen by the bond angle, which is imposed by the additional constraint of the chelate. An X-ray structural determination of a complex containing B has not been seen, and the chelating diazenido complexes are the closest example of this structural type. All of the structural examples of chelating diazenido complexes have an extended π-system in the ring containing the metal, and as a result, the metal-nitrogen bond is shortened from what might be expected in B.

A third structural type is the neutral diazene Γ, which is a two electron donor to the metal. Both the α-nitrogen and the β-nitrogen are substituted, and there is a double bond between the nitrogens. Electrons from the α-nitrogen are donated to the metal orbitals, and the charge on both nitrogens is neutral, resulting in an overall neutrally charged ligand. The metal-nitrogen bond lengths are about 1.9 Å, indicative of some multiple bonding, which results from the delocalization of the π-system of the ligand. The nitrogen-nitrogen bond lengths are about 1.3 Å, which is demonstrative of multiple bonding. As would be expected, these bond lengths are longer than those found in diazenido complexes due to the change in hybridization of the α-nitrogen. Again, the chelating diazene ligands present an additional constraint to the system. The chelation forces Γ to have the substituents on the α-nitrogen and the β-nitrogen in a *trans* configuration. There is one example of a monodentate diazene complex, $[Tc(CO)_3(PPh_3)_2(HNN(p\text{-}{}^tBu(C_6H_4))][PF_6]$.[1] This complex was synthesized from the diazonium salt, which inserts into a metal-hydride bond, instead of from the organohydrazine. The lack of chelation will diminish the π-system and lengthen the metal-nitrogen bond compared to the chelated examples.

Structural type Δ displays multiple bonding between the metal and the α-nitrogen and between the two nitrogens. The β-nitrogen is disubstituted. Since there is multiple bonding present between the nitrogens, the charge on the β-nitrogen is positive. The α-nitrogen is unsubstituted, and its electrons are donated to the metal orbitals forming a double bond to the metal, which gives this nitrogen an overall negative charge. As a result of the negatively charged α-nitrogen and the positively charged β-nitrogen, this zwitterionic ligand form is neutral. Generally, these metal-nitrogen bond lengths are between 1.75 and 1.9 Å. The nitrogen-nitrogen bond shows multiple bond character with lengths in the range of 1.24 to 1.33 Å, and the geometry is nearly linear with metal-nitrogen-nitrogen bond angles ranging from 160 to 174°. This structural type is referred to as a hydrazido(2-) ligand in the literature, which causes confusion in the assignment of oxidation states. Another, perhaps more appropriate, name seen in the literature is the isodiazene ligand.

The metal-nitrogen-nitrogen bond angle of the unsubstituted α-nitrogen and disubstituted β-nitrogen ligand tends to vary from nearly linear as in Δ to relatively bent as in E. The variance in the metal-nitrogen bond lengths and the bond angles is indicative of the degree of metal-nitrogen multiple bonding and the residence of the lone pair of the α-nitrogen. In the neutral E, the ligand has a metal-nitrogen single bond and a nitrogen-nitrogen double bond. A lone pair resides on the α-nitrogen, which is demonstrated by the protonation chemistry at this site to generate ligand form H.[2,3] The metal-nitrogen bond is shortened due to conjugation of the π-system throughout the ligand. A typical metal-nitrogen bond length is 1.9 Å, and a typical nitrogen-nitrogen bond length is approximately 1.2 Å. The ligand is bent, with typical metal-nitrogen-nitrogen bond angles in the 130 to 140° range, indicative of the sp^2 hybridization of the α-nitrogen. As expected, this structural type has longer metal-nitrogen bond lengths than Δ since it is more bent; however, the nitrogen-nitrogen bond length does not seem to vary as greatly from those of Δ.

Structural type Z has a metal-nitrogen single bond and a nitrogen-nitrogen single bond. Complexes with this uninegative ligand have metal-nitrogen bond lengths of about 2.2 Å and nitrogen-nitrogen bonds of about 1.4 Å. The metal-nitrogen-nitrogen bond angle is approximately

120°, indicative of the sp^3 hybridization of the nitrogens. Z is appropriately referred to as a uninegative ligand in the literature.

Structural type H can be considered as a substituted form of the neutral diazene Γ. Since the β-nitrogen is disubstituted, the overall ligand charge is unipositive. The metal-nitrogen bond length is between 1.9 and 2.0 Å, and the nitrogen-nitrogen bond length is approximately 1.3 Å. The metal-nitrogen bond is slightly shorter than a typical single bond due to some delocalization of the π-system of the ligand. The nitrogen-nitrogen bond length is indicative of multiple bonding. The metal-nitrogen-nitrogen bond angle is bent, ranging from 123 to 139°.

Structural type Θ, appropriately referred to as hydrazino, is a fully substituted, neutral organohydrazine behaving as a neutral donor ligand such as an amine ligand. Typical bond lengths are about 2.2 Å for the metal-nitrogen bond and 1.4 Å for the nitrogen-nitrogen bond. The metal-nitrogen-nitrogen bond angle is bent at approximately 120°, indicative of the sp^3 hybridization of the nitrogens.

There are some ambiguities with respect to the designation of a structural type in a complex if sufficient spectroscopic data do not exist. For example, if the substituent on the α- or the β-nitrogen is a hydrogen which is not found crystallographically, then simple examination of the bond lengths and angles will not suffice to determine the ligand type. Comparison of bond lengths and angles of the diazenido, A, to the isodiazene, Δ, shows that there is no way to discern between the two types on this basis. A case in point is the complex $ReCl_2(PPh_3)_2(NNHC(O)Ph)(HNNHC(O)Ph)$.[4,5] In the report of this complex, the formulation is ligands of the types Δ and Z, which places a hydrogen on the β-nitrogen (Δ) and hydrogens on the α- and β-nitrogens (Z). However, in the absence of sufficient spectroscopic data, the argument for the complex's containing ligands A and Θ can be made, placing all three hydrogens on one of the organohydrazide ligands.[6] As is the case with A and Δ, the bond lengths and angles of Z and Θ do not allow for differentiation between the two. The similar complex $ReCl_2(PPh_3)_2(NNC(O)Ph)(H_2NNHC(S)Ph)$[6] has been reported as consisting of organohydrazide types A and Θ. Since in both of the above-mentioned complexes there are insufficient data to determine conclusively which structural types are present, this paper classifies the complexes as they appear in the literature.

Additionally, an ambiguity can exist in the classification of types Γ and E by X-ray data when the substituents on the nitrogens are hydrogens and no additional spectroscopic data exist. An example of this dilemma is found in the complex $HB(pz)_3ReO(HNNC_8H_5N_2)$.[7] In the report of this complex, the hydrogen is not placed definitively on the α- or the β-nitrogen. The only spectroscopic evidence given for this hydrogen is a resonance in the ^1H NMR spectrum at 12 ppm. The bond lengths and angles of the two possible types, Γ and E, do not allow for an assignment to be made; however, the oxidation state assignment of the metal in either case should be rhenium(III) instead of rhenium(V) since both Γ and E are neutral. In some complexes, the placement of the hydrogen can be made using ^1H NMR data. In the case of $[Re(HNNpy)(NNpy)(PMe_2Ph)_2Cl][Cl]$,[8] the resonance for the α-nitrogen proton is found at 19 ppm, which indicates that this proton is deshielded and resides close to the metal. In addition, a COSY NMR experiment shows no coupling to this resonance.

Many of the problems in assigning the charge of some types of the organohydrazide ligand can be attributed to treating the organohydrazine as a redox inactive species. Since the reaction of the organohydrazine with a metal complex is a redox reaction, the loss of hydrogens from the hydrazine to form the hydrazide cannot be considered as a simple deprotonation, and therefore, the charge on the organohydrazide ligand cannot be assigned simply as a function of the number of hydrogens lost. The assignment of the charge by counting the number of hydrogens lost from the organohydrazine to form the organohydrazide accounts for much of the confusion in the charge assignment for many of the organohydrazide ligand forms shown in Figure 1. Since organohydrazines are reducing, all of the electrons forming the metal-nitrogen bond can be considered to be derived from the organohydrazine. In addition, the nitrogen is more electronegative than the metal, and when considering the charge assignments of the ligands, the electrons, by definition, should be assigned to the more electronegative element. Some additional examples and inconsistencies found in the literature are given below.

Structural type A is found in a number of complexes in the literature. (See Table 1.) An early example is the rhenium diazenido complex, $Re(NNPh)(PMe_2Ph)_3Cl_2$,[9,10] which is formed from the reaction of $Re(PMe_2Ph)_3Cl_3$ and phenylhydrazine. The diazenido complex is correctly assigned as rhenium(III), and the metal nitrogen bond is described as a σ-and a π-donation to the metal center. This assignment is based on the X-ray structural determination, which found that the rhenium-nitrogen bond length is 1.80 Å, consistent with π-orbital interaction between the nitrogen and the metal orbitals.[11] The nitrogen-nitrogen bond length of 1.23 Å is consistent with a double bond.

Starting from $ReOCl_3(PPh_3)_2$, trigonal bipyramidal complexes, $Re(NNC_6H_4Br)_2(PPh_3)_2L$, where L = Cl, SAr, with two uninegative diazenido ligands have been made.[12] The rhenium-nitrogen bond lengths are 1.798(19) Å and 1.730(13) Å, and the nitrogen-nitrogen bond lengths are 1.241(29) Å and 1.324(17) Å, respectively. As a result, the formal oxidation state of rhenium in these complexes should be assigned as +3. The analogous $Tc(NNC_6H_4Br)_2(PPh_3)_2Cl$ has also been synthesized and assigned as technetium(I) by Nicholson *et al.*[13] The technetium-nitrogen bond length is 1.796(6) Å, and the nitrogen-nitrogen bond length is 1.229(9) Å. The bond lengths of all of these complexes demonstrate multiple bonding character throughout the diazenido unit. The formal oxidation state of the metal should be assigned as +3, as is the assignment made by Dilworth *et al.* of $Tc(III)(NNC_6H_4Cl)_2(PPh_3)_2Cl$.[14]

Similar octahedral complexes can also be made using potentially chelating organohydrazines. (See Table 2.) An example is $ReCl_2(PPh_3)_2(NNC_8H_5N_2)$, which has been assigned in its report as rhenium(V) due to the designation of the diazenido unit as a 3- ligand.[5] Instead, the designation of the diazenido ligand as a 1- ligand makes the formal oxidation state of the complex rhenium(III). The rhenium-nitrogen bond length in this complex is 1.79(2) Å, and the nitrogen-nitrogen bond length is 1.29(2) Å. These lengths demonstrate the multiple bond character of the metal-nitrogen bond and the multiple bond character of the nitrogen-nitrogen bond. The chelating diazenido forms an extended π-system with the metal center, and complexes of this type have non-contact shifted NMR spectra.[8,15]

Summary

X-ray structural data have been applied in the classification of the structural forms found on the Group 7 organohydrazide complexes. The degree of substitution and the degree of multiple bonding between the metal and the α-nitrogen and the α- and the β-nitrogen, in most cases, can be determined from the structural data. The organization of these complexes on this basis creates a uniform way of characterizing and discussing this class of compounds. Although not all instances have been addressed by this survey, a rational basis for discussion of this chemistry has been presented.

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Table 1: Diazenido A complexes

Complex	**M=N**NR bond length (Å)	M**N=N**R bond length (Å)	**M=N=N**R bond angle (°)
$\mathrm{Re(NNPh)(PMe_2Ph)_3Cl_2}$[9,10]	1.80	1.23	172
$\mathrm{[(\eta^5\text{- }Cp^*)Mn(\mathit{o}\text{-}N_2C_6H_4CF_3)(CO)_2][BF_4]}$[16]	1.693(7)	1.211(8)	171.8(8)
$\mathrm{Re(PPh_3)(S(CH_2)_2S(CH_2)_3S(CH_2)_2S)(NNCOPh)}$[17,18]	1.776(12)	1.267(17)	167.5(12)
$\mathrm{ReBr_2(\mathbf{NNPh})(NNHPh)(PPh_3)_2}$[19]	1.793(11)	1.212(16)	172.4(10)
$\mathrm{[HNEt_3][Re_2(NNPh)_2(SPh)_7]}$[20]	1.81(2)	1.23(3)	170.0(18)
	1.81(2)	1.24(3)	171.4(19)
$\mathrm{ReCl_2(PPh_3)_2(NNCO_2Me)(O_2)}$[21]	1.798(40)	1.108(56)	170.2(22)
$\mathrm{Re(NNC_6H_4Br)_2(PPh_3)_2Cl}$[12]	1.798(19)	1.241(29)	172.0(27)
$\mathrm{Re(NNC_6H_4Br)_2(PPh_3)_2SAr}$[12]	1.730(13)	1.324(17)	160.9(2)
	1.798(16)	1.249(23)	178.1(2)
$\mathrm{Tc(NNC_6H_4Br)_2(PPh_3)_2Cl}$[13]	1.796(6)	1.229(9)	170.7(7)
$\mathrm{ReCl_2(PPh_3)_2(NCMe)(NNCOPh)}$[5]	1.756(7)	1.25(1)	172.1(6)
$\mathrm{ReCl_2(PPh_3)_2(NNCO_2Ph)(C_5H_5N)}$[5]	1.72(2)	1.28(2)	166.9(12)
$\mathrm{ReCl_2(PPh_3)_2(\mathbf{NNC(O)Ph})(H_2NNHC(S)Ph)}$[6]	1.712(17)	1.267(24)	170.5(16)
$\mathrm{ReCl_2(PPh_3)_2(\mathbf{NNC(O)Ph})(H_2NNHC(O)SMe)}$[6]	1.732(3)	1.248(5)	172.0(3)

$[Et_4N][Re(NNPh)_2(O_2C_6H_4)_2]$[22]	1.825(11)	1.21(2)	163.9(9)
	1.809(9)	1.21(1)	170.0(9)
$[Re(HNNpy)(\mathbf{NNpy})(PMe_2Ph)_2Cl][Cl]$[8]	1.802(7)	1.221(9)	172.0(9)
$Re(\mathbf{NNC_4H_2N_2CF_3})(HNNC_4H_2N_2CF_3)(PPh_3)Cl_2$	1.756(9)	1.267(12)	173.2(8)
$Re(HNNpy)(\mathbf{NNpy})(PPh_3)Cl_2$[23]	1.778(14)	1.212(22)	172.8(13)
$Re(HNNpy)(\mathbf{NNpyH})Cl_3$ [24]	1.741(7)	1.253(12)	168.1(8)
$[Re(p\text{-}NNC_6H_4Me)_2(dmpe)_2][PF_6]$[25]	1.909(2)	1.223(3)	162.7(2)

Table 2: Chelating diazenido complexes

Complex	**M=N**NR bond length (Å)	M**N=N**R bond length (Å)	**M=N=N**R bond angle (°)
$ReCl_2(PPh_3)_2(NNCOPh)$[5]	1.769(8)	1.30(2)	133.8(7)
$ReCl_2(PPh_3)_2(NNC_8H_5N_2)$[5]	1.79(2)	1.29(2)	136.4(9)
$TcCl_2(PPh_3)_2(NNC_8H_5N_2)$[26]	1.767(12)	1.274(17)	138.6(7)
$Re(NNpy)(PPh_3)_2Cl_2$[8]	1.815(8)	1.256(12)	137.3(7)
$Tc(NNC_4H_2N_2CF_3)(PPh_3)_2Cl_2$[15]	1.810(8)	1.267(10)	138.0(6)

Table 3: Diazene Γ complexes

Complex	**M-N**HNR bond length (Å)	M-H**N=N**R bond length (Å)	**M**-H**N=N**R bond angle (°)
Re(HNNC(S)Ph)$_3$* • DMF[27]	2.003(13)	1.336(16)	127.8(8)
	1.994(12)	1.338(17)	N/A
	2.002(9)	1.365(16)	N/A
Re(HNNC(S)Ph)$_3$• OPPh$_3$[27]	1.959(6)	1.333(8)	131.0(6)
ReO(**HNNC(S)Ph**)(HNNHC(S)Ph)[6]	2.022(9)	1.350(12)	124.2(6)
[Re(**HNNC(S)Ph**)(HNNHC(S)Ph)$_2$][Cl][27]	2.009(18)	1.347(21)	127.0(13)
HB(pz)$_3$ReO(HNNC$_8$H$_5$N$_2$)[7]	1.935(7)	1.400(12)	121.0(6)
[Re(**HNNpy**)(NNpy)(PMe$_2$Ph)$_2$Cl][Cl][8]	1.949(9)	1.319(11)	126.4(7)
Re(NNC$_4$H$_2$N$_2$CF$_3$)(**HNNC$_4$H$_2$N$_2$CF$_3$**)(PPh$_3$)Cl$_2$[15]	1.937(9)	1.322(13)	129.0(7)
Re(**HNNpy**)(NNpyH)Cl$_3$[24]	1.936(10)	1.309(11)	127.1(8)
Re(**HNNpy**)(NNpy)(PPh$_3$)Cl$_2$[23]	1.915(21)	1.340(26)	130.9(16)
[Tc(CO)$_3$(PPh$_3$)$_2$(HNN(*p*-^{t}Bu(C$_6$H$_4$)][PF$_6$]**[1]	2.157(6)	1.243(8)	124.2(5)

* It is unclear whether all three of the organohydrazide ligands are protonated since the complex is paramagnetic. DMF is interacting with the organohydrazide ligand or ligands, which makes the placement of the proton or protons ambiguous. Molybdenum tris(thiobenzoyl)diazene complexes were prepared, and an X-ray crystal structure was reported.[28] In this case, the DMF is not interacting with the diazene ligands.

** This is the only non-chelating diazene structure, and as a result, the metal-nitrogen bond is elongated because the π-system is not as extended as in the chelated examples.

Table 4: Isodiazene Δ complexes

Complex	**M=N**NR$_2$ bond length (Å)	M=**N=N**R$_2$ bond length (Å)	**M=N=N**R$_2$ bond angle (°)
[ReCl$_2$(NH$_3$)(NNHPh)(PMe$_2$Ph)$_2$][Br][10]	1.750(12)	1.28(2)	172(1)
ReCl$_2$(PPh$_3$)$_2$(**NNHCOPh**)(HNNHCOPh)[4,5]	1.730(7)	1.275(9)	174.3(6)
ReCl$_2$(PPh$_3$)$_2$(**NNHCOPh**)(HNNHCOMe)[5]	1.712(7)	1.27(1)	172.2(7)
[Re(NNMePh)$_2$(S$_2$CNMe$_2$)$_2$][BPh$_4$][29]	1.78(1)	1.29(1)	166.6(8)
	1.777(9)	1.30(1)	166.9(9)
[Et$_4$N][Re(NNPh$_2$)$_2$(O$_2$C$_6$H$_4$)$_2$][22]	1.770(12)	1.33(2)	159.6(8)
	1.768(10)	1.32(2)	159.7(8)

Table 5: E complexes

Complex	**M-N**-NR$_2$ bond length (Å)	M-**N**-**N**R$_2$ bond length (Å)	**M**-**N**-**N**R$_2$ bond angle (°)
(η^5- Cp)Re(CO)$_2$(*p*-NN(CH$_3$)C$_6$H$_4$OMe)[2]	1.937(7)	1.283(10)	138.1(6)
ReBr$_2$(NNPh)(**NNHPh**)(PPh$_3$)$_2$[19]	1.922(11)	1.287(15)	131.2(10)*
ReO(NNMePh)(SPh)$_3$[12]	1.858(9)	1.255(15)	145.6(10)
[ReOCl(NNMePh)(PPh$_3$)$_2$][PF$_6$]$_2$[29]	1.845(6)	1.261(8)	146.3(4)

* There is hydrogen bonding between a bromine and the β-nitrogen proton, which causes the bond angle to be lessened.

Table 6: Z complexes

Complex	**M-N**R-NR$_2$ bond length (Å)	M-**N**R**-N**R$_2$ bond length (Å)	**M**-**N**R-**N**R$_2$ bond angle (°)
$ReCl_2(PPh_3)_2$(NNHCOPh)(**HNNHCOPh**)[4,5]	2.212(8)	1.44(1)	119.5(4)
$ReCl_2(PPh_3)_2$(NNHCOPh)(**HNNHCOMe**)[5]	2.206(8)	1.441(9)	121.3(5)

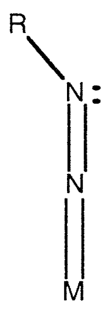
Table 7: H complexes

Complex	$\mathbf{M\text{-}N}R{=}NR_2$ bond length (Å)	$M\text{-}\mathbf{NR{=}N}R_2$ bond length (Å)	$\mathbf{M}\text{-}\mathbf{N}R{=}\mathbf{N}R_2$ bond angle (°)
$[(\eta^5\text{- Cp})Re(CO)_2(p\text{-}HNN(CH_3)C_6H_4Me)][BF_4]$[3]	1.949(9)	1.32(1)	139.1(7)
ReO(HNNC(S)Ph)(**HNNHC(S)Ph**)[6]	2.054(7)	1.379(9)	122.3(5)
[Re(NHNC(S)Ph)(**HNNHC(S)Ph**)$_2$][Cl][27]	1.965(18)	1.397(21)	127.3(12)
	1.989(15)	1.376(20)	123.0(12)

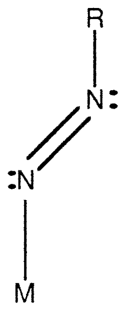
Table 8: Hydrazino Θ complexes

Complex	**M-N**R_2-NR_2 bond length (Å)	M-**N**R_2**-N**R_2 bond length (Å)	**M-N**R_2-**N**R_2 bond angle (°)
$ReCl_2(PPh_3)_2(NNC(O)Ph)(\mathbf{H_2NNHC(S)Ph})$[6]	2.224(17)	1.427(20)	119.9(11)
$ReCl_2(PPh_3)_2(NNC(O)Ph)(\mathbf{H_2NNHC(O)SMe})$[6]	2.192(4)	1.421(5)	119.6(3)

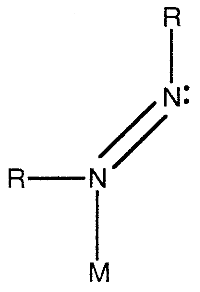
Figure 1: The Structural Types of Organohydrazide Ligands. The uninegative, linear, four electron donor diazenido A; the uninegative, bent, one electron donor diazenido B; the neutral, bent, two electron donor diazene Γ; the zwitterionic, neutral, bent, four electron donor isodiazene Δ; the neutral, bent, one electron donor E; the uninegative, bent, one electron donor Z; the unipositive, bent, one electron donor H; the neutral, bent, two electron donor, hydrazino Θ.



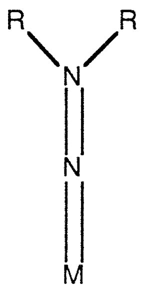
A



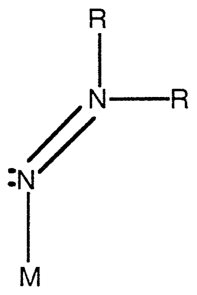
B



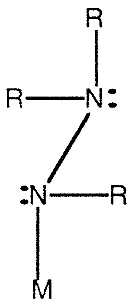
Γ



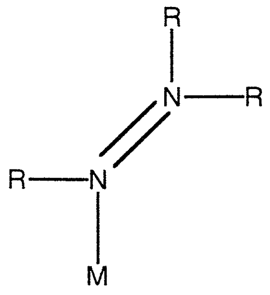
Δ



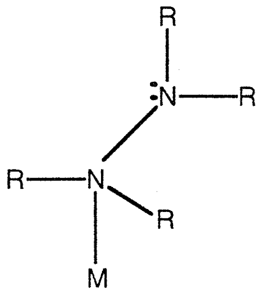
E



Z



H



Θ

CHAPTER 2

Technetium(III) and Rhenium(III) Organohydrazide Complexes from 2-Hydrazinopyridine

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Introduction

Organohydrazines are good reducing agents, and the coordination chemistry of organohydrazides, where an organohydrazide is defined as any ligand derived from an organohydrazine, is of interest because organohydrazides are structurally versatile ligands. The coordination chemistry of organohydrazides[1] has been studied for some time, especially as models for intermediates for the reduction of dinitrogen to ammonia.[2-9] Of interest is the group VII coordination chemistry of organohydrazides.[10-15] In particular, the chemistry of organohydrazides coordinated to technetium or rhenium is important since they can serve to link important biomolecules to these metals for use as radiopharmaceuticals.[16] The organohydrazines can be derivatized, thus allowing the chemical properties of the metal-organohydrazide complex to be altered to manipulate biodistributions. In addition, the reducing nature of organohydrazines and their reactivity with metal-oxo groups makes them ideal candidates for use with existing radiopharmaceutical kits that frequently employ technetium-oxo complexes.

As a potentially chelating organohydrazide ligand, 2-hydrazinopyridine provides the opportunity for additional modes of binding to the metal center. In our studies, we have seen the organohydrazide exhibit two binding modes and two sites of protonation. Depending on the degree of protonation, the oxidation state of the ligand is either -1 or neutral. The ligand also can bind as a chelating ligand or as a linear one. Reported here is a new form, the unprotonated chelate, diazenido (1-). (See Figure 1.)

Experimental

Caution! ^{99}Technetium is a weak β-emitter (E = 0.292 MeV, $t_{1/2} = 2.12 \times 10^5$ years). All work has been done in laboratories approved for the use of low levels of radioactive materials. Precautions have been detailed elsewhere.[17]

Ammonium pertechnetate was supplied as a gift from DuPont Biomedical Products. Reagents and solvents were used as received unless otherwise specified. ^{1}H and ^{31}P{^{1}H} NMR spectra were recorded on a Varian XL-300 or Varian Unity-300 FTNMR spectrometer. The chemical shifts are referenced to the residual proton impurity in the deuterated solvent. ^{31}P{^{1}H} chemical shifts are reported relative to an external standard of 85% H_3PO_4. Fast atom bombardment mass spectra of samples dissolved in *p*-nitrobenzylalcohol matrix were recorded with a Finnigan MAT 8200 mass spectrometer equipped with an Ion Tech FAB gun operating at an accelerated voltage of 8 kV. The FAB gun produced a beam of 6-8 keV xenon neutrals. Elemental analyses were performed by Atlantic Microlab, Norcross, GA.

Syntheses. The complexes $ReO(PPh_3)_2Cl_3$,[18] $Re(N)(PPh_3)_2Cl_2$,[19] $Re(MeCN)(PPh_3)_2Cl_3$,[20] and $Tc(MeCN)(PPh_3)_2Cl_3$[21] were prepared by the literature methods.

Preparation of $Re(NNpy)(PPh_3)_2Cl_2$ (1). To 0.1116 g (0.1340 mmol) of $ReO(PPh_3)_2Cl_3$ and approximately 10 mL of methanol in a 100 mL rounded bottom flask was added 0.0528 g (29.0 mmol) of 2-hydrazinopyridine dihydrochloride (HYPY· 2HCl). The flask was equipped with a condenser, and the reaction mixture was refluxed for seven hours. A deep pink solid precipitated, which was filtered on a fritted glass funnel (porosity E) and washed with methanol. The solid was dried *in vacuo*. Yield 0.0534 g (45%). The solid was recrystallized from CH_2Cl_2 layered with methanol to yield X-ray quality crystals. The X-ray structure analysis revealed one-half of a methanol molecule in the lattice.

Anal. Calc. for $C_{41}H_{34}Cl_2N_3P_2Re$: C, 55.47; H, 3.86; Cl, 7.99; N, 4.73. Found: C, 55.06; H, 3.89; Cl, 7.93; N, 4.67.

^1H NMR (CD_2Cl_2) δ (ppm) 7.5-7.2 (m); 7.15 (t); 6.8(d); 6.1 (t).

$^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ (ppm) -4.69.

FABMS(+) {in *p*-nitrobenzylalcohol} 887.6 m/z.

Method 2: To a 100 mL rounded bottom flask containing 0.0471 g (0.259 mmol) HYPY·2HCl in approximately 5 mL of methanol was added 0.1003 g (0.1261 mmol) $Re(N)Cl_2(PPh_3)_2$ along with an additional 5 mL of methanol. The reaction mixture was heated to reflux for one hour, and the solid that precipitated was filtered and dried as above. The solid was spectroscopically identical to the solid obtained by Method 1 as determined by FABMS(+) {in *p*-nitrobenzylalcohol}. Yield 0.0134 g (12%).

Method 3: The same procedure as above can be followed starting with $Re(MeCN)Cl_3(PPh_3)_2$ to give a spectroscopically identical material as determined by ^1H NMR spectroscopy. Yield 40%.

Preparation of $[Re(HNNpy)(NNpy)(PMe_2Ph)_2Cl]^+[Cl]^-$ (2). To a 100 mL rounded bottom flask containing 0.1045 g (0.2066 mmol) of $Re(HNNpy)(NNpyH)Cl_3$[22] and 5 mL methanol was added 0.50 mL (3.5 mmol) PMe_2Ph. Additional methanol was added, and the reaction mixture was stirred for two days. The reaction mixture was filtered on a fritted glass funnel (porosity E). The red filtrate was collected, and the volume reduced *in vacuo* to approximately 1 mL. Ether was added, and a red-brown solid precipitated. The solvent was removed *in vacuo*, and enough methanol necessary to dissolve the solid was added along with ether. The solution was cooled, and the red-brown solid was filtered and dried *in vacuo*. Yield 0.0638 g (41%). The solid was recrystallized from methanol and ether to yield X-ray quality crystals. The X-ray structure analysis revealed a chlorine counter ion in the lattice.

^{1}H NMR (CD_2Cl_2) δ (ppm) 19 (br); 8.6 (d); 8.45 (d); 8.0 (d); 7.95 (t); 7.9 (t); 7.3 (m); 7.2 (t); 7.1 (m); 6.8 (m); 1.7 (t); 1.6 (t).

$^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ (ppm) -16.69.

FABMS(+) {in *p*-nitrobenzylalcohol} 711.4 m/z.

Preparation of $Tc(NNpy)(PPh_3)_2Cl_2$ (3). A 50 mL rounded bottom flask containing 0.09967 g (0.1294 mmol) $Tc(MeCN)(PPh_3)_2Cl_3$, 0.07372 g (0.09563 mmol) HYPY· 2HCl, and 25 mL MeOH was refluxed for 6 hours. A pink solid precipitated, which was filtered on a fritted glass funnel (porosity E). The solid was washed with methanol and dried *in vacuo*. Yield 0.04553 g (60%). The solid can be recrystallized from CH_2Cl_2/Et_2O or toluene/pentane. An X-ray structural determination was attempted, but due to a packing disorder in two different sets of crystals, only the connectivity of **(3)** was able to be determined. The connectivity is consistent with what is reported here.

Anal. Calc. for $C_{41}H_{34}Cl_2N_3P_2Tc$: C, 61.52; H, 4.28; N, 5.25. Found: C, 61.40; H, 4.37; N, 4.80.

^{1}H NMR (CD_2Cl_2) δ (ppm) 7.7 (d); 7.5 (d); 7.5-7.0 (m); 6.85 (d); 6.2 (t).

FABMS(+) {in *p*-nitrobenzylalcohol} 799.2 m/z.

Preparation of [Tc(phen)(HNNpy)(NNpy)Cl][Cl] (4). To a 50 mL rounded bottom flask equipped with a stir bar 0.06393 g (0.1954 mmol) $TcO_3(phen)Cl$[23] and 7 mL methanol were added. To this solution, 0.14789 g (0.81236 mmol) HYPY· 2HCl dissolved in approximately 10 mL methanol was added. The reaction mixture was heated for one hour, yielding a red-brown solution. The solution was filtered after cooling to room temperature, and a small amount of dark red-brown solid was recovered. This solid was identified as $Tc(HNNpy)(NNpyH)Cl_3$.[22] The filtrate was reduced in volume to approximately one milliliter, and a large amount of ether was added. A red-brown solid precipitated. The solid was filtered and dried *in vacuo*. Yield 0.04971 g (45%).

^{1}H NMR (CD_2Cl_2) δ (ppm) 18.7 (br) (α-nitrogen proton).

FABMS(+) {in *p*-nitrobenzylalcohol} 527.0 m/z.

IR(KBr) (cm^{-1}) ν (Tc=N) 1246 (vs).

Preparation of Tc(HNNpy)(NNpyH)Cl$_3$ from [TBA][TcOCl$_4$]. To a 50 mL rounded bottom flask equipped with a stir bar, 0.09786 g (0.1962 mmol) [TBA][TcOCl$_4$] and 10 mL methanol were added. To this solution, 0.07278 g (0.3999 mmol) HYPY· 2HCl and 10 mL methanol were added. The color changed immediately to dark green. The reaction was stirred at room temperature for two days, and a dark precipitate was present and filtered. The complex was identified to be Tc(HNNpy)(NNpyH)Cl$_3$ by ^{1}H NMR spectroscopy. Yield 0.05789 g (70%).

Reaction of Tc(HNNpy)(NNpyH)Cl$_3$ with PPh$_3$. To a 50 mL rounded bottom flask equipped with a stir bar, 0.04790 g Tc(HNNpy)(NNpyH)Cl$_3$ and 10 mL methanol were added. To the reaction mixture, 0.06804 g PPh$_3$ and 15 mL methanol were added. The reaction mixture was heated for one hour, at which time five drops of N,N-diisopropylethylamine were added. Heating was continued for an additional two hours. The reaction mixture was filtered, and a pink solid was isolated. This solid was identified to be Tc(N)(PPh$_3$)$_2$Cl$_2$ by IR spectroscopy. Yield 40%.

Preparation of Re(O)(OMe)(py)$_2$Cl$_2$. To a 100 mL rounded bottom flask, 0.1027 g (0.1511 mmol)*trans*-Re(O)$_2$(py)$_4$PF$_6$ and 10 mL methanol were added. To the reaction mixture, 0.0311 g (0.1708 mmol) HYPY· 2HCl was added. The reaction mixture was stirred at room temperature for 20 minutes and was heated for 1.5 hours, at which time a purple solid had precipitated out of the dark reaction mixture. The bright purple solid was filtered on a fritted disc, washed with methanol, and dried *in vacuo*. The complex was identified by ^{1}H NMR and mass spectroscopies. Yield 0.02095 g (30%).

Reactions using 6, 6'-dihydrazino 2, 2'-bipyridine; 2, 9-dihydrazino 1, 10-phenanthroline;[24] and 2, 6-dihydrazinopyridine. Reactions with a variety of technetium and rhenium starting materials were attempted as above using the disubstituted hydrazine ligands; however, the products obtained were not analogous to the monosubstituted hydrazinopyridine. For technetium, in the presence of phosphine, the complex $Tc(N)(PPh_3)_2Cl_2$ was obtained. The ligands tend to react as most organohydrazines do to form the nitrido species. For rhenium, in the presence of phosphine, the complex $Re(PPh_3)_2Cl_4$ was obtained. It is interesting to note here the differences in the reduction chemistry of technetium and rhenium. When starting with perrhenate or pertechnetate to which HCl was added, the reactions yielded a brown precipitate that was soluble only in DMSO and DMF, and no ^{1}H NMR spectrum was observed. Mass spectral analysis did not yield any discernible fragments.

Ligand Syntheses

The ligand 6, 6'-dihydrazino 2, 2'-bipyridine was prepared starting from 6, 6'-dichloro 2, 2'-bipyridine in a similar manner to methods found in the literature, which start from 6, 6'-dibromo 2, 2'-bipyridine;[25-27] however, the solution needs to be refluxed overnight. ^{1}H NMR (d_6-DMSO) δ (ppm) 7.6-7.5 (m, 4H), 7.4 (s, 2H, NH), 6.7 (d, 2H), 4.2 (br, 4H, NH_2). These resonances are assigned differently than those reported previously.[25] The synthesis of 6, 6'-dichloro 2, 2'-bipyridine appears in the literature by different methods.[28,29]

Preparation of 6, 6'-dichloro 2,2'-bipyridine. To a 100 mL rounded bottom flask, 1.1579 g (6.1528 mmol) of 2, 2'-bipyridine N, N'-dioxide and 0.71 g (3.4 mmol) of PCl_5 were added along with 15 mL $POCl_3$. The mixture was refluxed under an atmosphere of argon for two hours. The solvent was removed *in vacuo*. Ice and water were added until no further reaction occurred, and the white precipitate was filtered and dried *in vacuo*. Yield 0.3469 g (25%). ^{1}H NMR ($CDCl_3$) δ (ppm) 8.35 (d, 2H), 7.8-7.7 (t, 2H), 7.35 (d, 2H). The resonances reported previously omit the triplet found at 7.8-7.7 ppm.[29]

Preparation of 2, 6-dihydrazinopyridine. This complex was prepared in a similar manner to the disubstituted bipyridine starting from 2, 6-dibromopyridine.

X-Ray Crystallographic Data Collection Parameters.

The data for **(1)** and **(2)** were collected using a Siemens platform goniometer with a CCD detector using molybdenum Kα radiation ($\lambda = 0.71073$ Å). The data for **(1)** were collected using a crystal having dimensions 0.2 x 0.08 x 0.08 mm. The crystal system was triclinic, a = 10.5549(7) Å, b = 12.2699(8) Å, c = 16.8206(12) Å, and α = 105.9050(10)°, β = 95.8930(10)°, γ = 111.0100(10)°, leading to a cell volume V = 1906.1(2) Å^3 with $Z = 2$. The space group was found to be $P\bar{1}$. The absorption coefficient was 3.322 mm^{-1}, the extinction coefficient was 0.0082(9), the calculated density ρ = 1.571 g/cm^3, and F(000) = 894. The data were obtained at 188(2) K in the θ range 1.29 to 23.34° with limiting indices $-11 \leq h \leq 10$, $-12 \leq k \leq 13$, $-16 \leq l \leq 18$. Of the 7684 reflections collected, 5273 were independent (R_{int} = 0.0920). The structure was solved by direct methods (SHELXTL v.5.0, Sheldrick, G. M. and Siemens Industrial Automation, Inc., 1995). Least squares refinement based upon F^2 with 5268 data, zero restraints, and 461 parameters converged with final residuals: R_1 = 0.0496, wR_2 = 0.1454, and GOF = 1.223 based upon $I > 2\sigma(I)$.

The data for **(2)** were collected using a crystal having dimensions 0.28 x 0.32 x 0.30 mm. The crystal system was orthorhombic, a = 17.383(4) Å, b = 13.967(3) Å, c = 12.002(2) Å, and $\alpha = \beta = \gamma = 90°$, leading to a cell volume V = 2913.9(10) Å^3 with $Z = 4$. The space group was found to be $Pna2_1$. The absorption coefficient was 4.490 mm^{-1}, the extinction coefficient was 0.0023(2), the calculated density ρ = 1.700 g/cm^3, and F(000) = 1468. The data were obtained at 296(2) K in the θ range 1.87 to 23.27° with limiting indices $-18 \leq h \leq 19$, $-14 \leq k \leq 15$, $-6 \leq l \leq 13$. Of the

11285 reflections collected, 3083 were independent ($R_{int} = 0.0448$). A semi-empirical absorption correction from Ψ scans was applied. The structure was solved by the Patterson method (SHELXTL v.5.0, Sheldrick, G. M. and Siemens Industrial Automation, Inc., 1995). Least squares refinement based upon F^2 with 3083 data, one restraint, and 335 parameters converged with final residuals: $R_1 = 0.0281$, $wR_2 = 0.0673$, and GOF = 1.227 based upon $I > 2\sigma(I)$.

Results and Discussion

Organohydrazines can react with group VII metal-oxo complexes to form metal-nitrido complexes or metal-imido complexes;[30-32] however, the organohydrazine, 2-hydrazinopyridine, reacts differently. In particular, 2-hydrazinopyridine has an additional mode of binding[14,33] that the similar phenylhydrazine does not possess.[12] The pyridine nitrogen gives the organohydrazide ligand the ability to form a chelate, which gives the ligand additional stability that may contribute to the unique reactivity of this hydrazine with metal synthons. One is the monodentate, linear organodiazenido. The second is as a bidentate chelate. In addition, the chelate is seen as a uninegative, unprotonated ligand or as a neutral ligand with the α-nitrogen protonated. The M(III) octahedral products formed in these reaction have unique electronic characteristics that can be seen in the ^{1}H NMR spectra. The binding of the pyridine nitrogen to the metal to form the chelate may account for the diamagnetic behavior of the complexes formed.

The electronic characteristics may be attributed to the π-system formed by the chelate in which the lone pair of electrons is donated by the pyridine nitrogen into the t_{2g} set of the metal. This donation allows the M(III) product to behave as a diamagnetic pseudo-M(I) complex. This diamagnetic behavior is seen in the ^{1}H NMR spectra of these d^4 octahedral complexes. For complexes **(1)**, **(2)**, and **(3)**, the sharp pyridyl proton resonances are seen in the 6 to 8 ppm range, which is where they are expected to be in a diamagnetic complex. In contrast, the octahedral, Tc(III) complex, $Tc(py)_3Cl_3$, has pyridyl resonances ranging from 23.44 ppm to -17.88 ppm.[34] These organohydrazide complexes should not be assigned to the +5 oxidation state in order to account for their diamagnetic behavior due to the reducing nature of the hydrazine. A hydrazine, here, is a two electron reductant, and in order for it to bind as an organohydrazide, it must be oxidized either by the metal center or an external oxidant. As a result, the reactions in which synthons starting at the +7 oxidation state that react to contain two organohydrazides must account for a four electron reduction to arrive at the +3 state.[22,35]

The reactivity of 2-hydrazinopyridine with metal synthons seems to follow a general pattern. First, for each hydrazine that binds to the metal center as an organohydrazide ligand, a two electron reduction occurs. Second, the final oxidation state of the product is +3. When M(VII) species are reacted, the products contain two organohydrazide ligands, which result in an overall four electron reduction to the M(III) products. This trend is similar to that found in the tris-diazene Tc(I) and Re(I) chelate complexes in which three hydralazines react with the metal center to result in an overall six electron reduction of the metal center from M(VII) to M(I).[14] When the Re(V) species $ReO(PPh_3)_2Cl_3$ is reacted with an excess of 2-hydrazinopyridine dihydrochloride, the product contains one organohydrazide ligand forming $Re(NNpy)(PPh_3)_2Cl_2$ **(1)**. (See Scheme 1.) In this case, a two electron reduction to the M(III) product has occurred. Interestingly, **(1)** can also be synthesized from $ReN(PPh_3)_2Cl_2$. In addition, $Tc(MeCN)(PPh_3)_2Cl_3$ reacts to form the one organohydrazide-containing Tc(III) product, **(3)**, in the presence of excess 2-hydrazinopyridine dihydrochloride; the acetonitrile may be reduced in order for the hydrazine to undergo the two electron oxidation necessary for binding to the metal center. The acetonitrile must be bound as a ligand to the metal in order for the metal-organohydrazide complex to form. Reactions attempted using other Re(III) synthons in acetonitrile led to no reaction and recovery of the starting materials. The analogous $Re(MeCN)(PPh_3)_2Cl_3$ also reacts to form **(1)**.

The X-ray structural determinations of **(1)** and **(2)** reveal that the coordinated hydrazide ligands have multiple bonding character. The diazenido(1-) chelate of **(1)** has Re-N1 bond length of 1.815(8) Å, a N1-N2 bond length of 1.256(12) Å, and a Re-N3 bond length of 2.174(8) Å suggesting that multiple bonding is present throughout the chelate ring. The same feature is seen in the neutral organodiazene chelate in the X-ray structural determination of **(2)**, which has a Re-N22 bond length of 1.949(9) Å, a N22-N23 bond length of 1.319(11) Å, and a Re-N21 bond length of 2.167(7) Å. Evidence for a hydrogen bound to the α-nitrogen (N22) is found in the ^{1}H NMR, which has a resonance at 19 ppm that integrates to be equal to one proton. A COSY NMR spectrum shows no coupling to the resonance at 19 ppm. The bonds of the chelated organohydrazide of **(1)** and **(3)** are shorter than those of the chelate in **(2)**. The shorter bonds are a result of the anionic nature of the chelate in **(1)** and **(3)** versus the neutral chelate in **(2)**. In addition to the chelate found in **(2)**, there is a monodentate organodiazene ligand with a short N11-

N12 bond length of 1.221(9) Å and a short Re-N11 bond length of 1.802(7) Å, which suggest multiple bond character in the ligands. The organodiazene of **(2)** is relatively linear with a Re-N11-N12 bond angle of 172.0(9)°, which makes it unlikely that the resonance found at 19 ppm in the ^{1}H NMR is due to a hydrogen bound to N11.

Complex **(4)** contains two organohydrazide ligands, the monodentate organohydrazide and the neutral α-nitrogen protonated diazene chelate, similar to **(2)**. The α-nitrogen proton resonance is found at 18.7 ppm in the ^{1}H NMR spectrum. Complex **(4)**, in which the technetium has a formal oxidation state of +3, is prepared from the Tc(VII) starting material, TcO_3(phen)Cl. Two organohydrazide ligands are present on **(4)**, and an overall four electron reduction of technetium has occurred. As is the case for complexes **(1)**, **(2)**, and **(3)**, complex **(4)** has a diamagnetic ^{1}H NMR spectrum that has aryl resonances from 10 to 6 ppm. A by-product of the formation of **(4)** is Tc(HNNpy)(NNpyH)Cl_3. The by-product is formed in a low yield and is easily separated from **(4)** due to the lack of solubility of Tc(HNNpy)(NNpyH)Cl_3 in methanol.

As shown in Table 12, the bond lengths and angles of complex **(1)** are very similar to the rhenium[33] and technetium[15] hydralazine (1-hydrazinophthalazine, $C_8H_5N_4$) complexes, despite the fact that these complexes are assigned to the +5 oxidation state.[14] In comparison, the bond lengths of the neutral, bidentate organohydrazide ligands are consistently longer than the anionic, bidentate form of the ligand, which is as expected. In each of the cases shown in Table 6, the β-nitrogen displays sp^2 hybridization, which is reflected in the bond angles. In addition, the metal-nitrogen-nitrogen bond angles of the terminal organodiazenido ligands are nearly linear with a slight deviation in the case of the zwitterionic, monodentate organodiazenido ligand.

The reaction of Tc(NNpyH)(HNNpy)Cl_3 with triphenylphosphine is not analogous to the reaction of Re(NNpyH)(HNNpy)Cl_3 with triphenylphosphine.[35] In the rhenium reaction, Re(PPh_3)(HNNpy)(NNpy)Cl_2 is formed. In the case of technetium, the nitrido complex, Tc(N)$(PPh_3)_2Cl_2$, is formed. This reaction is the only one in which the otherwise stable pyridyl-hydrazide core has been removed from the metal center.

Not all metal-oxo complexes react to form the metal-organohydrazide complex. The reaction of $Re(O)_2(py)_4PF_6$ with hydrazinopyridine is an example. In this case, the hydrazine reacts with the rhenium complex to yield $Re(O)(OMe)(py)_2Cl_2$. There is no formation of the metal-organohydrazide complex. The use of the organohydrazine as a reductant of the metal center in which the corresponding organohydrazide complex is not formed is seen in the reactions with the dihydrazino ligands, 6, 6'-dihydrazino 2, 2'-bipyridine; 2, 9-dihydrazino 1, 10-phenanthroline; and 2, 6-dihydrazinopyridine. The reason that the chelate complexes are not formed with these ligands is probably due to the presence of the second hydrazine on the ligand and not due to the bite angle of the ligand since the three disubstituted ligands vary in angle. Reactions with a mono-hydrazine substituted bipyridine would be useful in order to determine if the additional chelation can be formed with the metal center since the dihydrazinobipyridine does not.

Conclusion

The organohydrazine 2-hydrazinopyridine reacts with rhenium(V), rhenium(III), technetium (VII) and technetium(III) synthons to form metal-organohydrazide complexes. The organohydrazine behaves as a formal two electron reductant. The resulting organohydrazide complexes have unique electronic characteristics that allow them to exhibit diamagnetic behavior despite being d^4 octahedral complexes. These characteristics seem to be due to the π-system formed by the chelated organohydrazide.

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Table 1: Crystallographic Data for (**1**) ·1/2 MeOH and (**2**).

Complex	$C_{41.50}H_{34}Cl_2N_3O_{0.5}P_2Re$	$C_{26}H_{30}Cl_2N_6P_2Re$
Molecular weight	901.76	745.60
Wavelength	0.71073 Å, Mo Kα	0.71073 Å, Mo Kα
Temperature, K	188(2)	296(2)
Crystal system	Triclinic	Orthorhombic
Crystal dimensions	0.2 x 0.08 x 0.08 mm	0.28 x 0.32 x 0.30 mm
Space group	$P\bar{1}$	$Pna2_1$
a, Å	10.5549(7)	17.383(4)
b, Å	12.2699(8)	13.967(3)
c, Å	16.8206(12)	12.002(2)
α, °	105.9050(10)	90
β, °	95.8930(10)	90
γ, °	111.0100(10)	90
V, $Å^3$	1906.1(2)	2913.9(10)
Z	2	4
Density (calculated), g/cm^3	1.571	1.700
Absorption coefficient, mm^{-1}	3.322	4.490
F(000)	894	1468
Diffractometer	Siemens SMART/CCD	Siemens SMART/CCD
Scan Type	ω Scans	ω Scans
θ range for data collection (°)	1.29 to 23.34	1.87 to 23.27
Limiting Indicies	$-11 \le h \le 10$, $-12 \le k \le 13$, $-16 \le l \le 18$	$-18 \le h \le 19$, $-14 \le k \le 15$, $-6 \le l \le 13$
Reflections Collected	7684	11285
Unique data	5268	3083

Max. and Min. Transmission	0.6355 and 0.4050	0.2934 and 0.2227
Refinement Method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/ restraints/ parameters	5268 / 0 / 461	3083 / 1 / 335
Goodness of Fit on F^2	1.223	1.227
Final R indicies $[I>2\sigma(I)]$	$R1 = 0.0496$	$R1 = 0.0281$
	$wR2 = 0.1454$	$wR2 = 0.0673$
R indices (all data)	$R1 = 0.0650$	$R1 = 0.0384$
	$wR2 = 0.1713$	$wR2 = 0.0840$
Extinction Coefficient	0.0082(9)	0.0023(2)
Largest diff. peak and hole	2.959 and -2.097 eÅ^{-3}	0.618 and 0.576 eÅ^{-3}

Table 2: Atomic Coordinates (x 10^4) and Equivalent Isotropic Displacement Parameters ($Å^2$ x 10^3) for **(1)**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Re	2864(1)	2046(1)	2222(1)	24(1)
Cl(2)	1789(3)	125(2)	1088(2)	34(1)
Cl(1)	5051(3)	1908(3)	2512(2)	40(1)
P(1)	3818(2)	3222(2)	1296(2)	26(1)
P(2)	2132(3)	941(2)	3233(2)	29(1)
N(3)	879(8)	2182(7)	1947(5)	28(2)
N(1)	2889(8)	3435(7)	2977(5)	28(2)
N(2)	2037(9)	3909(9)	3162(5)	40(2)
C(21)	511(11)	982(9)	3503(7)	33(2)
C(1)	813(10)	3170(8)	2545(6)	29(2)
C(41)	4941(10)	4827(10)	1889(6)	33(2)
C(51)	4884(10)	2724(11)	604(6)	36(2)
C(46)	5879(11)	5096(11)	2639(7)	43(3)
C(42)	4991(11)	5808(10)	1602(7)	40(2)
C(52)	6089(11)	3596(11)	504(7)	40(2)
C(41)	1705(11)	3940(12)	897(7)	43(3)
C(5)	-354(12)	3428(12)	2516(8)	48(3)
C(11)	2499(10)	3351(11)	568(6)	38(3)
C(3)	-1406(11)	1736(12)	1214(7)	46(3)
C(31)	3408(11)	1607(10)	4242(6)	35(2)
C(22)	-668(11)	439(10)	2867(8)	41(3)
C(66)	2788(12)	-1080(11)	2610(7)	41(3)
C(61)	1828(10)	-692(9)	2961(6)	30(2)

C(54)	6392(13)	1991(13)	-529(8)	49(3)
C(53)	6830(12)	3200(12)	-61(8)	48(3)
C(56)	4451(12)	1488(11)	127(7)	46(3)
C(62)	724(12)	-1542(11)	3145(8)	45(3)
C(6)	-230(10)	1501(10)	1283(6)	37(2)
C(55)	5184(15)	1132(13)	-449(8)	55(3)
C(42)	628(12)	3979(10)	385(8)	44(3)
C(63)	588(13)	-2729(11)	2987(8)	52(3)
C(43)	313(12)	3405(12)	-472(8)	53(3)
C(42)	6829(12)	6310(12)	3087(8)	55(3)
C(4)	-1491(12)	2679(13)	1847(8)	52(3)
C(13)	1098(14)	2779(12)	-821(8)	53(3)
C(12)	2193(12)	2714(12)	-308(7)	49(3)
C(44)	5915(12)	7018(11)	2060(9)	52(3)
C(23)	-1897(13)	556(12)	3019(9)	53(3)
C(34)	5385(16)	2720(16)	5762(8)	72(4)
C(35)	4666(21)	1479(16)	5454(10)	89(6)
C(45)	6819(12)	7254(11)	2787(9)	54(3)
C(36)	3695(17)	895(13)	4692(9)	70(4)
C(26)	424(16)	1638(14)	4303(9)	65(4)
C(32)	4144(16)	2876(13)	4571(8)	74(5)
C(25)	-828(18)	1694(18)	4428(11)	86(5)
C(24)	-1965(16)	1157(17)	3790(12)	79(5)
C(33)	5122(19)	3443(15)	5324(9)	88(6)
C(64)	1572(14)	-3121(10)	2648(7)	48(3)
C(65)	2669(13)	-2290(12)	2463(7)	49(3)
C(7)	1211(47)	5257(36)	4890(34)	153(25)

O(7)	1752(34)	5132(30)	5653(14)	153(17)

Table 3: Atomic Coordinates (x 10^4) and Equivalent Isotropic Displacement Parameters (Å^2 x 10^3) for **(2)**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Re	1645(1)	1439(1)	2518(1)	31(1)
Cl(1)	2414(2)	1704(2)	870(2)	45(1)
P(1)	758(2)	610(2)	1265(2)	38(1)
P(2)	2648(2)	2313(2)	3534(3)	38(1)
N(11)	1031(4)	2478(5)	2528(11)	38(2)
N(12)	564(4)	3124(5)	2636(11)	41(2)
N(13)	13(5)	4553(6)	2100(9)	58(3)
N(21)	2218(4)	84(5)	2817(6)	33(2)
N(22)	1238(5)	936(5)	3914(8)	40(2)
N(23)	1436(6)	126(6)	4399(8)	49(2)
C(11)	346(6)	1404(7)	220(10)	40(3)
C(12)	647(7)	1515(8)	-830(11)	57(4)
C(13)	325(10)	2173(11)	-1571(12)	76(5)
C(14)	-277(9)	2717(11)	-1276(17)	81(5)
C(15)	-588(8)	2637(10)	-226(16)	78(5)
C(16)	-282(7)	1982(8)	506(12)	59(3)
C(17)	-62(6)	118(9)	1992(11)	62(3)
C(18)	1164(8)	-388(8)	481(14)	70(4)
C(21)	2503(6)	3603(6)	3364(10)	41(3)
C(22)	2893(6)	4105(7)	2561(17)	55(3)
C(23)	2719(7)	5083(8)	2391(17)	71(4)
C(24)	2150(8)	5509(9)	3005(15)	81(6)
C(25)	1745(7)	4997(9)	3776(13)	63(4)

C(26)	1928(7)	4043(8)	3963(11)	49(3)
C(27)	3623(6)	2042(8)	3113(12)	58(3)
C(28)	2656(7)	2089(8)	5015(11)	60(3)
C(111)	542(6)	3879(7)	1827(10)	38(3)
C(112)	987(7)	3918(8)	910(11)	50(3)
C(113)	893(8)	4672(8)	186(12)	72(4)
C(114)	363(7)	5349(8)	395(14)	67(4)
C(115)	-33(7)	5284(9)	1367(16)	79(5)
C(211)	1971(5)	-358(7)	3757(9)	35(2)
C(212)	2241(6)	-1258(7)	4082(12)	47(3)
C(213)	2746(6)	-1709(8)	3436(12)	51(3)
C(214)	3004(6)	-1273(6)	2462(21)	55(3)
C(215)	2750(5)	-376(7)	2194(9)	43(3)
Cl(2)	466(3)	2297(2)	5492(3)	76(1)

Table 4: Bond Lengths in Å of (**1**).

Re-N(1)	1.815(8)
Re-N(3)	2.174(8)
Re-Cl(2)	2.378(2)
Re-Cl(1)	2.385(2)
Re-P(1)	2.457(2)
Re-P(2)	2.472(2)
P(1)-C(41)	1.812(10)
P(1)-C(51)	1.835(10)
P(1)-C(11)	1.837(10)
P(2)-C(61)	1.825(10)
P(2)-C(21)	1.829(10)
P(2)-C(31)	1.828(10)
N(3)-C(6)	1.355(13)
N(3)-C(1)	1.375(12)
N(1)-N(2)	1.256(12)
N(2)-C(1)	1.391(14)
C(21)-C(22)	1.37(2)
C(21)-C(26)	1.40(2)
C(1)-C(5)	1.38(2)
C(41)-C(46)	1.40(2)
C(41)-C(42)	1.40(2)
C(51)-C(56)	1.38(2)
C(51)-C(52)	1.40(2)
C(46)-C(42)	1.40(2)
C(42)-C(44)	1.39(2)

C(52)-C(53)	1.39(2)
C(41)-C(11)	1.36(2)
C(41)-C(42)	1.38(2)
C(5)-C(4)	1.38(2)
C(11)-C(12)	1.41(2)
C(3)-C(4)	1.38(2)
C(3)-C(6)	1.37(2)
C(31)-C(36)	1.39(2)
C(31)-C(32)	1.38(2)
C(22)-C(23)	1.40(2)
C(66)-C(61)	1.38(2)
C(66)-C(65)	1.39(2)
C(61)-C(62)	1.39(2)
C(54)-C(55)	1.38(2)
C(54)-C(53)	1.35(2)
C(56)-C(55)	1.37(2)
C(62)-C(63)	1.36(2)
C(42)-C(43)	1.36(2)
C(63)-C(64)	1.40(2)
C(43)-C(13)	1.39(2)
C(42)-C(45)	1.39(2)
C(13)-C(12)	1.41(2)
C(44)-C(45)	1.36(2)
C(23)-C(24)	1.33(2)
C(34)-C(35)	1.35(2)
C(34)-C(33)	1.38(2)
C(35)-C(36)	1.38(2)

C(26)-C(25)	1.38(2)
C(32)-C(33)	1.37(2)
C(25)-C(24)	1.35(2)
C(64)-C(65)	1.37(2)
C(7)-O(7)	1.42(6)

Table 5: Bond Angles in degrees of (**1**).

N(1)-Re-N(3)	69.9(3)
N(1)-Re-Cl(2)	154.3(3)
N(3)-Re-Cl(2)	84.6(2)
N(1)-Re-Cl(1)	110.1(3)
N(3)-Re-Cl(1)	179.3(2)
Cl(2)-Re-Cl(1)	95.40(9)
N(1)-Re-P(1)	90.3(2)
N(3)-Re-P(1)	91.7(2)
Cl(2)-Re-P(1)	93.65(8)
Cl(1)-Re-P(1)	87.67(8)
N(1)-Re-P(2)	88.9(2)
N(3)-Re-P(2)	93.1(2)
Cl(2)-Re-P(2)	89.41(8)
Cl(1)-Re-P(2)	87.61(9)
P(1)-Re-P(2)	174.59(8)
C(41)-P(1)-C(51)	102.9(5)
C(41)-P(1)-C(11)	102.8(5)
C(51)-P(1)-C(11)	103.5(5)
C(41)-P(1)-Re	112.3(3)
C(51)-P(1)-Re	119.2(4)
C(11)-P(1)-Re	114.3(3)
C(61)-P(2)-C(21)	103.7(4)
C(61)-P(2)-C(31)	100.9(4)
C(21)-P(2)-C(31)	105.7(5)
C(61)-P(2)-Re	120.0(3)

C(21)-P(2)-Re	111.9(3)
C(31)-P(2)-Re	113.0(3)
C(6)-N(3)-C(1)	117.2(9)
C(6)-N(3)-Re	130.7(7)
C(1)-N(3)-Re	112.0(6)
N(2)-N(1)-Re	137.3(7)
N(1)-N(2)-C(1)	105.8(8)
C(22)-C(21)-C(26)	117.4(11)
C(22)-C(21)-P(2)	118.4(8)
C(26)-C(21)-P(2)	123.9(10)
N(3)-C(1)-N(2)	114.5(8)
N(3)-C(1)-C(5)	122.6(10)
N(2)-C(1)-C(5)	122.9(9)
C(46)-C(41)-C(42)	118.0(10)
C(46)-C(41)-P(1)	118.7(8)
C(42)-C(41)-P(1)	123.2(8)
C(56)-C(51)-C(52)	119.1(9)
C(56)-C(51)-P(1)	120.2(8)
C(52)-C(51)-P(1)	120.5(9)
C(42)-C(46)-C(41)	120.7(11)
C(44)-C(42)-C(41)	121.2(11)
C(51)-C(52)-C(53)	119.3(11)
C(11)-C(41)-C(42)	121.3(11)
C(4)-C(5)-C(1)	118.5(11)
C(41)-C(11)-C(12)	120.2(10)
C(41)-C(11)-P(1)	118.8(8)
C(12)-C(11)-P(1)	120.5(9)

C(4)-C(3)-C(6)	119.6(11)
C(36)-C(31)-C(32)	117.9(10)
C(36)-C(31)-P(2)	123.2(9)
C(32)-C(31)-P(2)	118.9(8)
C(23)-C(22)-C(21)	120.7(12)
C(61)-C(66)-C(65)	120.8(10)
C(62)-C(61)-C(66)	118.6(10)
C(62)-C(61)-P(2)	122.5(8)
C(66)-C(61)-P(2)	118.7(8)
C(55)-C(54)-C(53)	119.8(10)
C(54)-C(53)-C(52)	121.1(11)
C(55)-C(56)-C(51)	120.2(11)
C(63)-C(62)-C(61)	120.8(11)
N(3)-C(6)-C(3)	122.4(10)
C(54)-C(55)-C(56)	120.5(12)
C(41)-C(42)-C(43)	120.7(11)
C(62)-C(63)-C(64)	121.0(11)
C(42)-C(43)-C(13)	118.9(10)
C(45)-C(42)-C(46)	119.1(12)
C(3)-C(4)-C(5)	119.5(10)
C(43)-C(13)-C(12)	121.4(11)
C(13)-C(12)-C(11)	117.4(11)
C(45)-C(44)-C(42)	119.6(11)
C(24)-C(23)-C(22)	120.8(14)
C(35)-C(34)-C(33)	119.7(13)
C(34)-C(35)-C(36)	122.0(14)
C(44)-C(45)-C(42)	121.4(11)

C(31)-C(36)-C(35)	119.3(14)
C(21)-C(26)-C(25)	119.7(14)
C(33)-C(32)-C(31)	122.2(13)
C(24)-C(25)-C(26)	121.5(14)
C(23)-C(24)-C(25)	119.8(13)
C(34)-C(33)-C(32)	119(2)
C(65)-C(64)-C(63)	118.9(10)
C(64)-C(65)-C(66)	119.9(11)

Table 6: Bond Lengths in Å of (**2**).

Re-N(11)	1.802(7)
Re-N(22)	1.949(9)
Re-N(21)	2.167(7)
Re-Cl(1)	2.416(3)
Re-P(1)	2.445(3)
Re-P(2)	2.453(3)
P(1)-C(17)	1.807(11)
P(1)-C(11)	1.822(11)
P(1)-C(18)	1.823(12)
P(2)-C(27)	1.808(11)
P(2)-C(28)	1.805(13)
P(2)-C(21)	1.830(9)
N(11)-N(12)	1.221(9)
N(12)-C(111)	1.43(2)
N(13)-C(115)	1.35(2)
N(13)-C(111)	1.357(13)
N(21)-C(215)	1.352(12)
N(21)-C(211)	1.356(13)
N(22)-N(23)	1.319(11)
N(23)-C(211)	1.384(13)
C(11)-C(12)	1.37(2)
C(11)-C(16)	1.40(2)
C(12)-C(13)	1.40(2)
C(13)-C(14)	1.34(2)
C(14)-C(15)	1.38(2)

C(15)-C(16)	1.38(2)
C(21)-C(22)	1.37(2)
C(21)-C(26)	1.38(2)
C(22)-C(23)	1.41(2)
C(23)-C(24)	1.37(2)
C(24)-C(25)	1.37(2)
C(25)-C(26)	1.39(2)
C(111)-C(112)	1.35(2)
C(112)-C(113)	1.37(2)
C(113)-C(114)	1.34(2)
C(114)-C(115)	1.36(2)
C(211)-C(212)	1.397(14)
C(212)-C(213)	1.33(2)
C(213)-C(214)	1.39(2)
C(214)-C(215)	1.367(14)

Table 7: Bond Angles in degrees of (**2**).

N(11)-Re-N(22)	94.0(4)
N(11)-Re-N(21)	166.9(4)
N(22)-Re-N(21)	73.2(3)
N(11)-Re-Cl(1)	102.1(4)
N(22)-Re-Cl(1)	163.7(2)
N(21)-Re-Cl(1)	90.8(2)
N(11)-Re-P(1)	90.7(3)
N(22)-Re-P(1)	97.4(3)
N(21)-Re-P(1)	88.7(2)
Cl(1)-Re-P(1)	85.26(10)
N(11)-Re-P(2)	91.0(3)
N(22)-Re-P(2)	90.6(3)
N(21)-Re-P(2)	91.5(2)
Cl(1)-Re-P(2)	86.40(10)
P(1)-Re-P(2)	171.66(10)
C(17)-P(1)-C(11)	104.7(5)
C(17)-P(1)-C(18)	105.3(6)
C(11)-P(1)-C(18)	105.2(6)
C(17)-P(1)-Re	112.3(4)
C(11)-P(1)-Re	112.5(3)
C(18)-P(1)-Re	115.8(5)
C(27)-P(2)-C(28)	103.4(6)
C(27)-P(2)-C(21)	107.7(5)
C(28)-P(2)-C(21)	106.3(6)
C(27)-P(2)-Re	115.1(4)

C(28)-P(2)-Re	114.1(4)
C(21)-P(2)-Re	109.6(3)
N(12)-N(11)-Re	172.0(9)
N(11)-N(12)-C(111)	119.3(11)
C(115)-N(13)-C(111)	114.1(11)
C(215)-N(21)-C(211)	117.3(8)
C(215)-N(21)-Re	129.7(6)
C(211)-N(21)-Re	113.0(6)
N(23)-N(22)-Re	126.4(7)
N(22)-N(23)-C(211)	110.4(9)
C(12)-C(11)-C(16)	117.2(12)
C(12)-C(11)-P(1)	123.4(9)
C(16)-C(11)-P(1)	119.3(10)
C(11)-C(12)-C(13)	120.3(12)
C(14)-C(13)-C(12)	121.3(14)
C(13)-C(14)-C(15)	120(2)
C(16)-C(15)-C(14)	119(2)
C(15)-C(16)-C(11)	121.9(14)
C(22)-C(21)-C(26)	119.8(10)
C(22)-C(21)-P(2)	120.9(9)
C(26)-C(21)-P(2)	118.8(9)
C(21)-C(22)-C(23)	119.4(14)
C(24)-C(23)-C(22)	120(2)
C(25)-C(24)-C(23)	120.6(12)
C(24)-C(25)-C(26)	119.6(13)
C(21)-C(26)-C(25)	120.7(12)
C(112)-C(111)-N(13)	124.0(10)

C(112)-C(111)-N(12)	124.6(9)
N(13)-C(111)-N(12)	111.4(10)
C(111)-C(112)-C(113)	118.6(11)
C(114)-C(113)-C(112)	120.2(13)
C(113)-C(114)-C(115)	117.4(12)
N(13)-C(115)-C(114)	125.5(11)
N(21)-C(211)-N(23)	116.9(8)
N(21)-C(211)-C(212)	122.4(10)
N(23)-C(211)-C(212)	120.6(10)
C(213)-C(212)-C(211)	119.0(12)
C(212)-C(213)-C(214)	119.7(11)
C(215)-C(214)-C(213)	119.6(14)
N(21)-C(215)-C(214)	121.8(12)

Table 8: Anisotropic displacement parameters (Å^2 x 10^3) for (**1**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[(ha^*)^2U_{11} + ... + 2hka^*b^*U_{12}]$.

	U11	U22	U33	U23	U13	U12
Re	22(1)	26(1)	23(1)	9(1)	4(1)	7(1)
Cl(2)	37(1)	26(1)	32(1)	4(1)	7(1)	9(1)
Cl(1)	29(1)	46(2)	53(2)	24(1)	9(1)	17(1)
P(1)	26(1)	25(1)	28(1)	11(1)	9(1)	8(1)
P(2)	32(1)	27(1)	25(1)	11(1)	6(1)	9(1)
N(3)	25(4)	27(4)	30(4)	11(4)	9(3)	6(4)
N(1)	31(4)	14(4)	35(4)	8(3)	5(4)	7(3)
N(2)	44(5)	46(6)	26(4)	4(4)	8(4)	18(5)
C(21)	41(6)	22(5)	41(6)	14(4)	13(5)	14(4)
C(1)	41(6)	13(4)	41(6)	12(4)	16(5)	14(4)
C(41)	27(5)	38(6)	29(5)	11(4)	7(4)	9(4)
C(51)	28(5)	52(7)	33(5)	16(5)	15(4)	17(5)
C(46)	37(6)	36(6)	48(7)	14(5)	9(5)	5(5)
C(42)	37(6)	35(6)	47(6)	19(5)	10(5)	8(5)
C(52)	32(6)	39(6)	53(7)	18(5)	13(5)	16(5)
C(41)	29(5)	71(8)	35(6)	29(6)	15(5)	17(6)
C(5)	46(7)	55(8)	54(7)	23(6)	21(6)	24(6)
C(11)	22(5)	57(7)	29(5)	21(5)	10(4)	4(5)
C(3)	32(6)	65(8)	43(6)	27(6)	4(5)	16(6)
C(31)	36(6)	32(6)	31(5)	11(4)	-1(4)	9(5)
C(22)	39(6)	35(6)	54(7)	24(5)	13(5)	13(5)
C(66)	48(6)	43(7)	39(6)	19(5)	17(5)	21(5)
C(61)	38(5)	30(5)	20(5)	9(4)	1(4)	13(4)

C(54)	64(8)	71(9)	48(7)	35(7)	34(6)	49(7)
C(53)	37(6)	69(9)	61(7)	40(7)	26(6)	29(6)
C(56)	45(6)	40(7)	52(7)	15(6)	22(6)	13(5)
C(62)	40(6)	44(7)	54(7)	26(6)	10(5)	13(5)
C(6)	31(5)	36(6)	32(5)	11(5)	2(4)	3(5)
C(55)	83(9)	59(8)	45(7)	25(6)	35(7)	40(7)
C(42)	45(6)	34(6)	71(8)	32(6)	16(6)	26(5)
C(63)	53(7)	33(7)	60(8)	19(6)	15(6)	3(5)
C(43)	35(6)	59(8)	65(8)	35(7)	-9(6)	13(6)
C(42)	38(6)	44(7)	58(8)	7(6)	-4(6)	0(6)
C(4)	32(6)	75(9)	66(8)	37(7)	19(6)	27(6)
C(13)	66(8)	50(7)	36(6)	12(5)	-9(6)	22(7)
C(12)	39(6)	63(8)	32(6)	6(5)	1(5)	17(6)
C(44)	40(7)	38(7)	84(9)	29(6)	21(7)	14(6)
C(23)	42(7)	41(7)	81(9)	29(7)	21(6)	14(6)
C(34)	69(9)	99(13)	38(7)	16(8)	-13(6)	34(9)
C(35)	131(15)	69(11)	59(9)	6(8)	-38(10)	58(11)
C(45)	37(6)	30(6)	78(9)	14(6)	8(6)	0(5)
C(36)	98(11)	47(8)	54(8)	12(6)	-20(8)	31(8)
C(26)	77(10)	78(10)	47(7)	17(7)	27(7)	40(8)
C(32)	92(11)	49(9)	49(8)	23(7)	-26(7)	1(8)
C(25)	76(11)	102(14)	73(10)	8(10)	44(9)	38(10)
C(24)	53(9)	102(13)	102(13)	46(11)	41(9)	37(9)
C(33)	109(13)	59(10)	49(8)	17(7)	-15(8)	-10(9)
C(64)	74(8)	27(6)	50(7)	18(5)	14(6)	25(6)
C(65)	59(8)	52(8)	44(6)	16(6)	17(6)	29(6)
C(7)	124(33)	62(23)	196(47)	-46(26)	-110(34)	54(24)

O(7)	192(28)	177(28)	70(14)	-74(16)	-83(17)	167(26)

Table 9: Anisotropic displacement parameters ($Å^2$ x 10^3) for (**2**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[(ha^*)^2U_{11} + ... + 2hka^*b^*U_{12}]$.

	U11	U22	U33	U23	U13	U12
Re	37(1)	25(1)	32(1)	1(1)	4(1)	1(1)
Cl(1)	51(2)	45(2)	41(2)	7(1)	10(1)	0(1)
P(1)	44(2)	31(1)	39(2)	-5(1)	2(1)	-1(1)
P(2)	41(2)	36(2)	39(2)	0(1)	-2(1)	-3(1)
N(11)	44(4)	38(4)	31(4)	8(7)	-3(8)	-2(3)
N(12)	42(4)	37(4)	43(6)	9(7)	9(6)	7(3)
N(13)	58(5)	36(5)	80(8)	7(5)	15(5)	14(5)
N(21)	36(4)	31(4)	31(7)	2(4)	4(4)	0(3)
N(22)	40(5)	32(5)	47(6)	4(4)	6(5)	-9(4)
N(23)	70(6)	40(6)	36(6)	9(5)	4(5)	-10(5)
C(11)	42(6)	41(6)	37(7)	-1(5)	-4(5)	-6(5)
C(12)	55(7)	70(9)	47(8)	-18(7)	11(7)	-27(6)
C(13)	112(13)	82(10)	35(8)	14(8)	-15(9)	-45(10)
C(14)	69(10)	83(11)	89(14)	18(10)	-36(10)	-18(8)
C(15)	54(8)	74(10)	107(14)	29(10)	-7(9)	-2(7)
C(16)	62(8)	55(8)	60(9)	1(7)	-3(7)	3(6)
C(17)	47(6)	67(8)	71(9)	12(7)	4(7)	-11(6)
C(18)	77(9)	46(7)	86(11)	-26(8)	0(9)	7(7)
C(21)	45(6)	31(6)	48(7)	-5(5)	-16(6)	-11(5)
C(22)	57(6)	47(6)	62(7)	6(12)	5(11)	-10(5)
C(23)	73(8)	55(7)	85(12)	19(9)	-8(10)	-22(6)
C(24)	73(9)	36(7)	134(17)	-1(8)	-27(9)	1(7)
C(25)	71(9)	51(8)	67(10)	-2(7)	1(7)	11(6)

C(26)	57(7)	39(6)	51(8)	-7(6)	-6(6)	0(5)
C(27)	40(6)	61(8)	73(9)	-12(7)	-9(6)	-2(5)
C(28)	79(9)	51(7)	49(8)	-2(7)	-17(7)	-16(6)
C(111)	34(5)	24(5)	57(8)	-4(5)	9(6)	-4(4)
C(112)	52(7)	41(6)	58(8)	5(6)	6(7)	9(5)
C(113)	94(10)	53(7)	69(10)	21(8)	26(9)	15(7)
C(114)	69(8)	42(7)	91(11)	27(7)	27(9)	13(6)
C(115)	65(8)	47(8)	126(15)	15(9)	18(10)	22(6)
C(211)	34(5)	32(5)	39(7)	5(5)	6(5)	0(4)
C(212)	51(7)	35(6)	54(8)	13(6)	1(6)	-1(5)
C(213)	51(7)	37(6)	65(9)	11(6)	-2(7)	3(5)
C(214)	39(5)	40(6)	85(11)	-12(10)	-4(11)	8(4)
C(215)	41(6)	44(6)	45(8)	11(5)	10(5)	4(5)
Cl(2)	121(3)	52(2)	54(2)	-3(2)	36(2)	14(2)

Table 10: Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for (**1**).

	x	y	z	U(eq)
H(46A)	5869(11)	4447(11)	2845(7)	52
H(42A)	4384(11)	5643(10)	1086(7)	48
H(52A)	6397(11)	4451(11)	820(7)	48
H(41A)	1896(11)	4334(12)	1493(7)	52
H(5A)	-379(12)	4104(12)	2946(8)	58
H(3A)	-2157(11)	1251(12)	734(7)	56
H(22A)	-649(11)	-21(10)	2316(8)	49
H(66A)	3538(12)	-513(11)	2467(7)	49
H(54A)	6913(13)	1734(13)	-911(8)	59
H(53A)	7661(12)	3788(12)	-120(8)	58
H(56A)	3646(12)	884(11)	197(7)	55
H(62A)	55(12)	-1292(11)	3385(8)	54
H(6A)	-193(10)	836(10)	849(6)	44
H(55A)	4855(15)	288(13)	-795(8)	66
H(42B)	99(12)	4411(10)	631(8)	52
H(63A)	-186(13)	-3302(11)	3107(8)	62
H(43A)	-431(12)	3432(12)	-824(8)	64
H(42C)	7474(12)	6487(12)	3591(8)	66
H(4A)	-2323(12)	2815(13)	1823(8)	63
H(13A)	893(14)	2386(12)	-1418(8)	64
H(12A)	2705(12)	2258(12)	-545(7)	58
H(44A)	5916(12)	7678(11)	1868(9)	63
H(23A)	-2693(13)	202(12)	2566(9)	64

H(34A)	6069(16)	3094(16)	6279(8)	86
H(35A)	4833(21)	992(16)	5771(10)	107
H(45A)	7456(12)	8082(11)	3094(9)	64
H(36A)	3229(17)	18(13)	4478(9)	84
H(26A)	1222(16)	2043(14)	4759(9)	78
H(32A)	3967(16)	3374(13)	4267(8)	89
H(25A)	-887(18)	2122(18)	4978(11)	103
H(24A)	-2816(16)	1207(17)	3890(12)	95
H(33A)	5610(19)	4319(15)	5539(9)	106
H(64A)	1480(14)	-3949(10)	2549(7)	57
H(65A)	3348(13)	-2539(12)	2235(7)	59

Table 11: Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for (**3**).

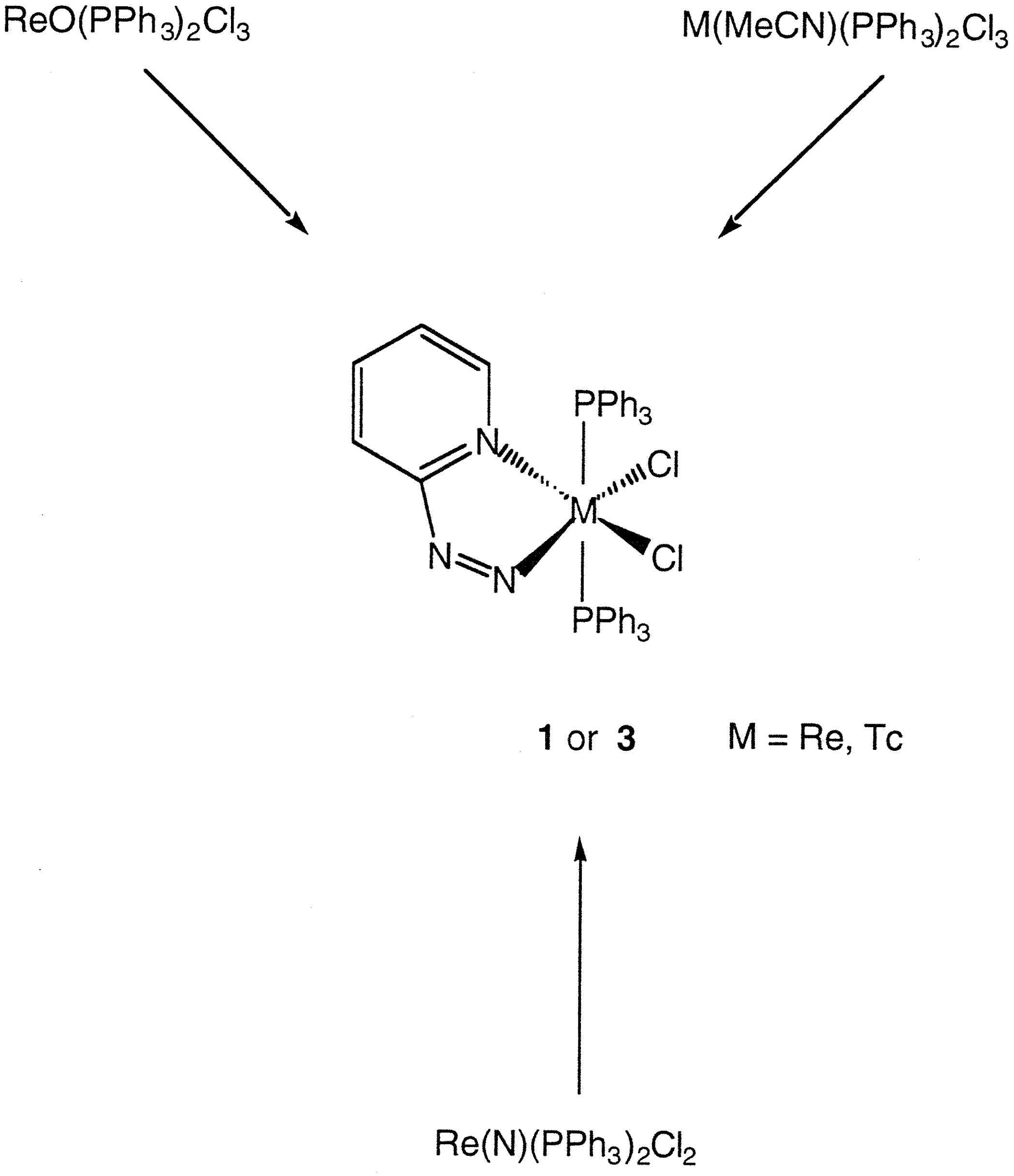
	x	y	z	U(eq)
H(12B)	1068(7)	1150(8)	-1049(11)	69
H(13B)	531(10)	2235(11)	-2282(12)	92
H(14A)	-485(9)	3150(11)	-1782(17)	97
H(15A)	-1001(8)	3020(10)	-15(16)	94
H(16A)	-498(7)	1922(8)	1212(12)	71
H(17A)	113(6)	-312(9)	2562(11)	74
H(17B)	-382(6)	-222(9)	1475(11)	74
H(17C)	-351(6)	629(9)	2326(11)	74
H(18A)	1606(8)	-173(8)	72(14)	83
H(18B)	785(8)	-631(8)	-28(14)	83
H(18C)	1314(8)	-887(8)	987(14)	83
H(22B)	3268(6)	3806(7)	2133(17)	66
H(23B)	2991(7)	5436(8)	1865(17)	85
H(24A)	2039(8)	6154(9)	2895(15)	97
H(25A)	1349(7)	5285(9)	4174(13)	75
H(26A)	1659(7)	3698(8)	4500(11)	58
H(27A)	3675(6)	2142(8)	2326(12)	70
H(27B)	3737(6)	1386(8)	3287(12)	70
H(27C)	3974(6)	2453(8)	3504(12)	70
H(28A)	2155(7)	2216(8)	5317(11)	72
H(28B)	3027(7)	2499(8)	5366(11)	72
H(28C)	2789(7)	1432(8)	5150(11)	72
H(11A)	1351(7)	3444(8)	769(11)	61

H(11B)	1197(8)	4713(8)	-449(12)	87
H(11C)	270(7)	5843(8)	-108(14)	81
H(11D)	-363(7)	5785(9)	1544(16)	95
H(21A)	2070(6)	-1538(7)	4740(12)	56
H(21B)	2926(6)	-2312(8)	3634(12)	61
H(21C)	3347(6)	-1590(6)	1996(21)	66
H(21D)	2949(5)	-74(7)	1567(9)	52

Table 12: Comparison of Bond Lengths and Angles of Organodiazenido and Organodiazene Ligands in Complexes of Rhenium and Technetium.

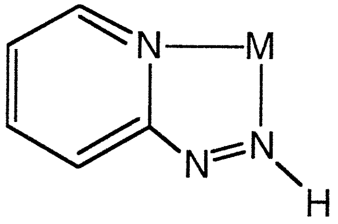
Complex	**M-N (Å)**	**N-N (Å)**	**M-N-N (°)**	**N-N-C (°)**
$\mathrm{Tc(C_8H_5N_4)Cl_2(PPh_3)_2}$[15]	1.767(12)	1.274(17)	138.6(7)	104.9(11)
	2.151(9)			
Re(hydralazine)$\mathrm{Cl_2(PPh_3)_2}$[33]	1.79(2)	1.29(2)	136.4(9)	106.0(14)
	2.14(2)			
Re(NNpy)$\mathrm{(PPh_3)_2Cl_2}$ **(1)**	1.815(8)	1.256(12)	137.3(7)	105.8(8)
	2.174(8)			
Re(HNNpy)(NNpyH)$\mathrm{Cl_3}$[22]	1.936(10)	1.309(11)	127.1(8)	109.7(9)
	2.164(7)			
	1.741(7)	1.253(12)	168.1(8)	115.8(10)
Re(HNNpy)(NNpy)$\mathrm{Cl_2(PPh_3)}$[35]	1.915(21)	1.340(26)	130.9(16)	106.8(17)
	2.147(15)			
	1.778(14)	1.212(22)	172.8(13)	120.9(16)
[Re(HNNpy)(NNpy)$\mathrm{(PMe_2Ph)_2Cl]^+}$ **(2)**	1.949(9)	1.319(11)	126.4(7)	110.4(9)
	2.167(7)			
	1.802(7)	1.221(9)	172.0(9)	119.3(11)

Reaction Scheme 1: Formation of M(NNpy)(PPh_3)$_2$$Cl_2$ (M = Tc, Re).

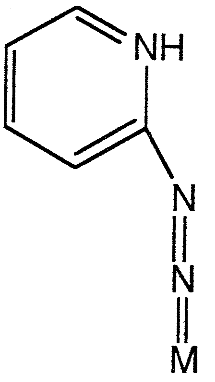

$ReO(PPh_3)_2Cl_3$
$M(MeCN)(PPh_3)_2Cl_3$
N
N
N
M
PPh_3
Cl
Cl
PPh_3
$Re(N)(PPh_3)_2Cl_2$

1 or **3**   M = Re, Tc

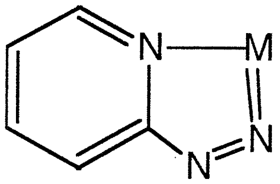
Figure 1: The neutral, organodiazene ligand (A); the neutral, but zwitterionic, diazenido ligand (B); the chelating diazenido(1-) ligand (C); and the terminal diazenido (1-) ligand (D).



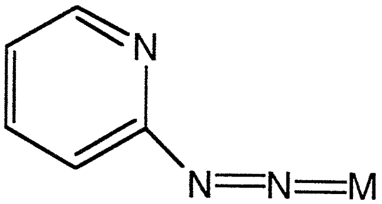
A



B



C



D

Figure 2: ORTEP of Re(NNpy)$(PPh_3)_2Cl_2$ with 35% ellipsoids.

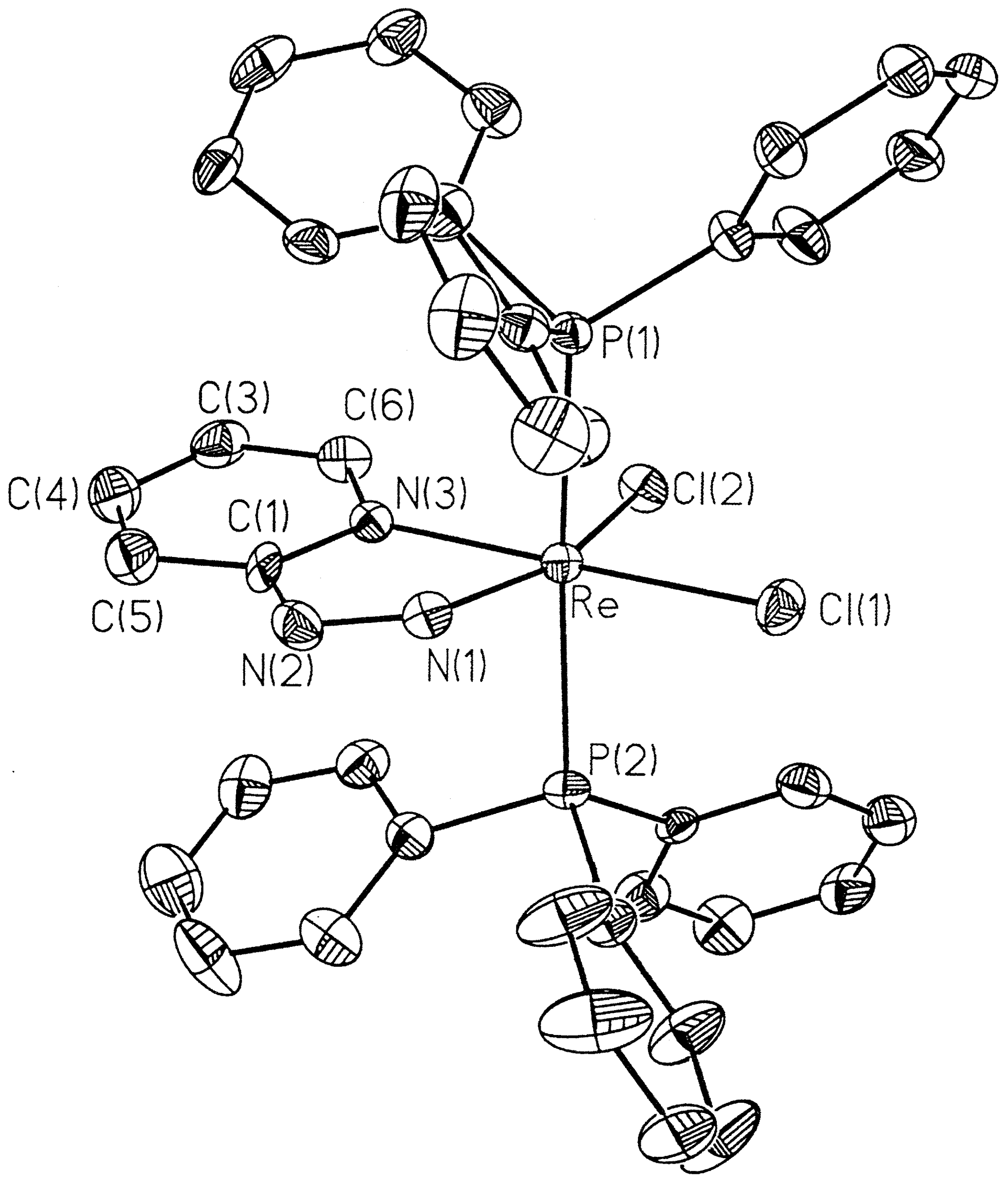

P(1)
C(3)
C(6)
C(4)
N(3)
Cl(2)
C(1)
Re
Cl(1)
C(5)
N(2)
N(1)
P(2)

Figure 3: ORTEP of [Re(HNNpy)(NNpy)(PMe_2Ph)$_2$Cl][Cl] with 35% ellipsoids.

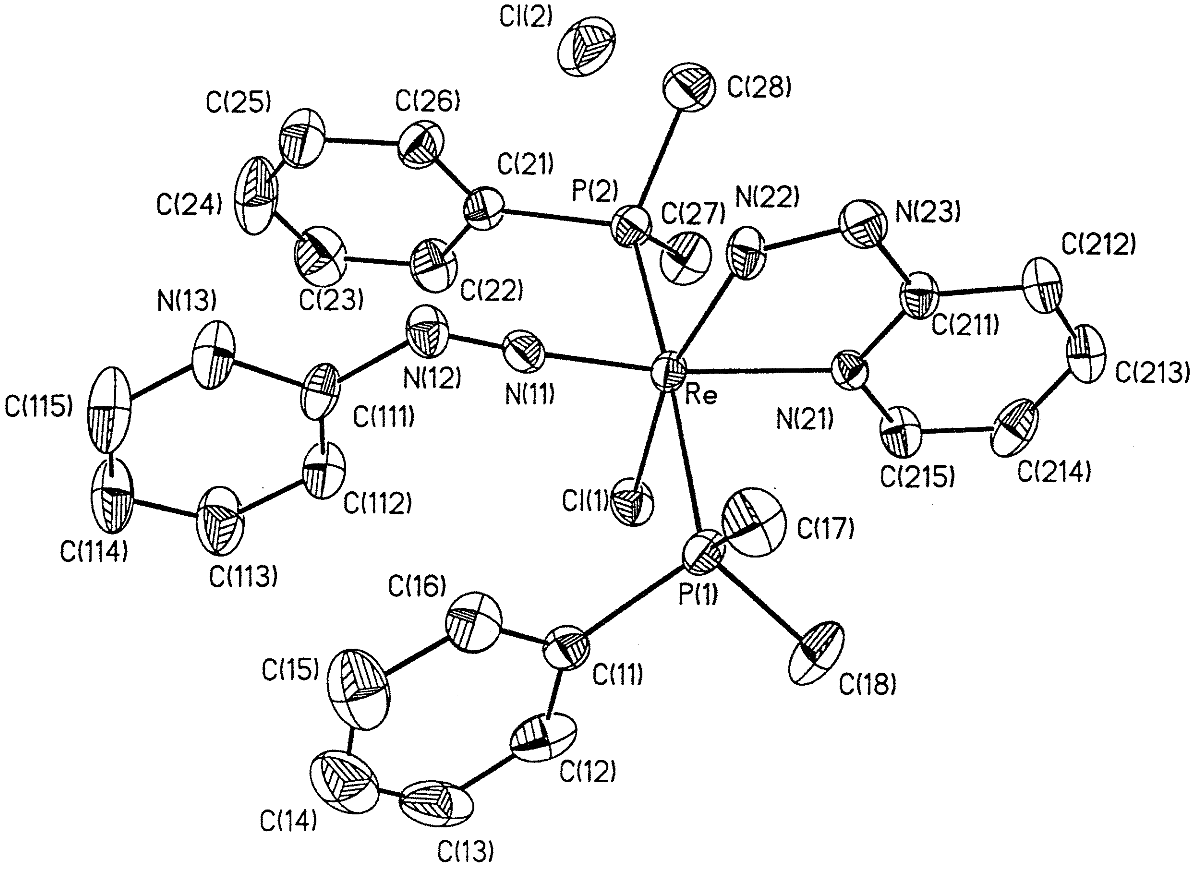

Cl(2)
C(28)
C(25)
C(26)
C(21)
P(2)
C(24)
C(27)
N(22)
N(23)
C(212)
C(23)
C(22)
N(13)
C(211)
N(12)
N(11)
Re
C(213)
C(115)
C(111)
N(21)
C(215)
C(214)
C(112)
Cl(1)
C(17)
C(114)
C(113)
C(16)
P(1)
C(15)
C(11)
C(18)
C(12)
C(14)
C(13)

Figure 4: ^{1}H NMR Spectrum of Re(NNpy)(PPh$_3$)$_2$Cl$_2$.

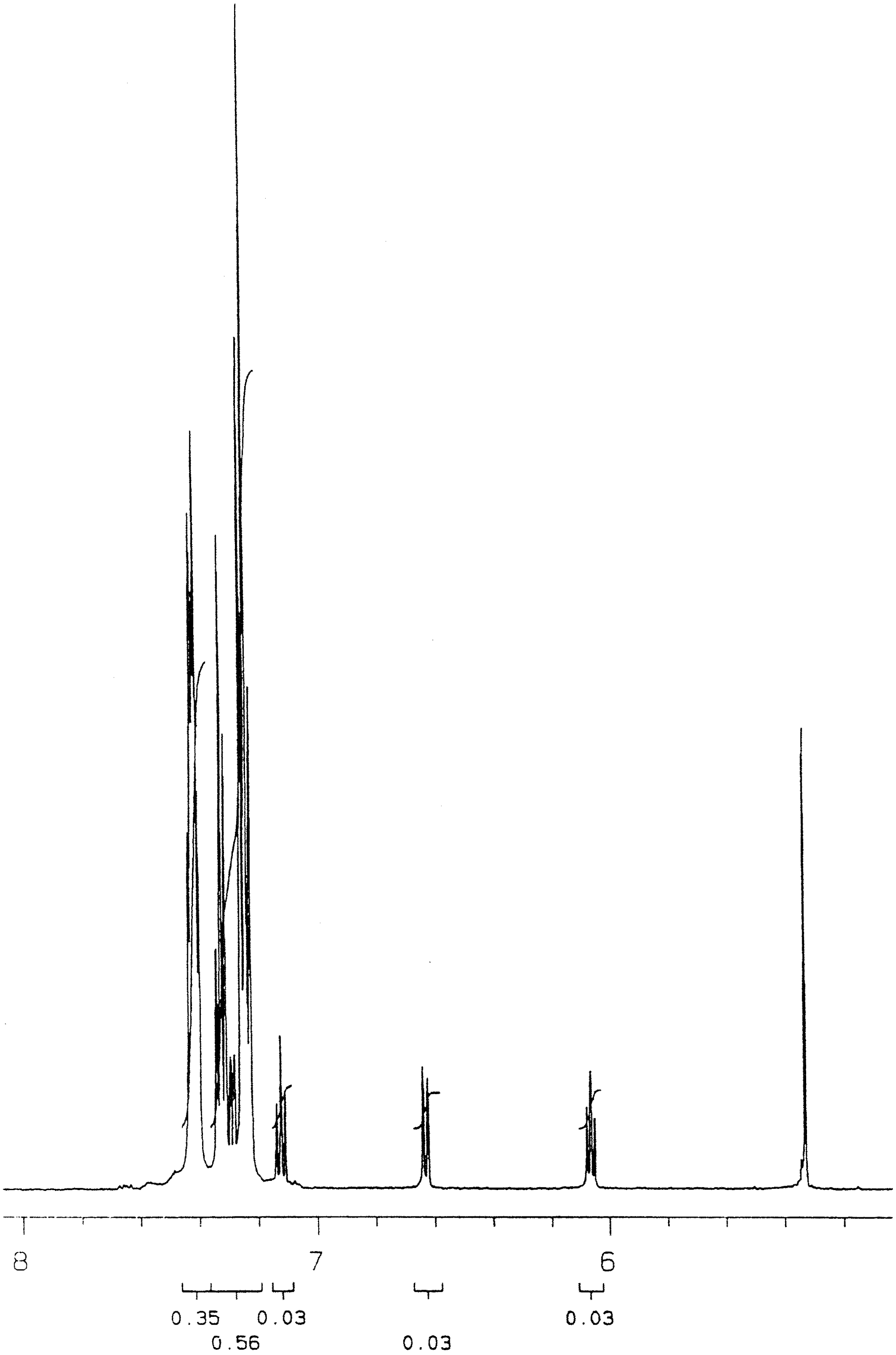
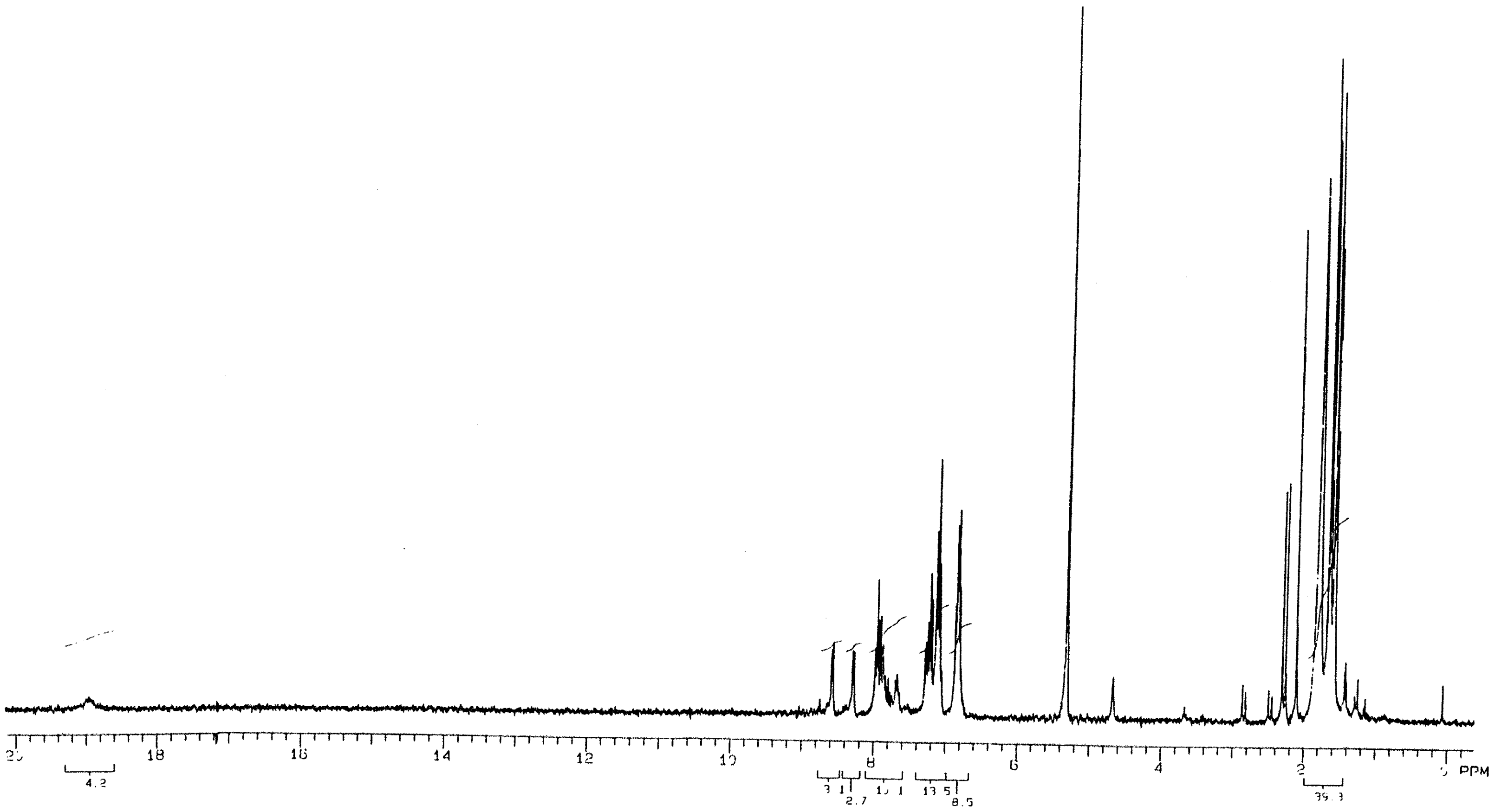

8
7
6
0.35
0.03
0.56
0.03
0.03

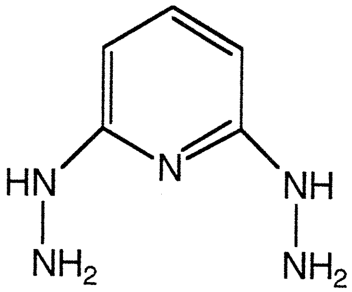
Figure 5: ^{1}H NMR Spectrum of [Re(HNNpy)(NNpy)(PMe_2Ph)$_2$Cl][Cl].

The α-N proton can be seen at 19 ppm.

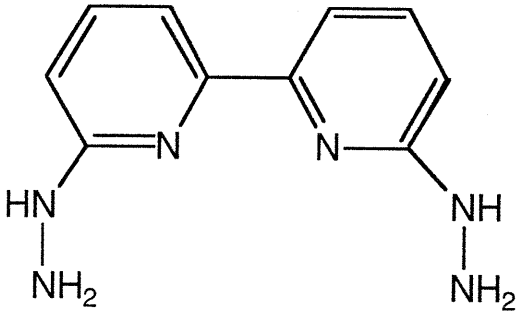


20
18
16
14
12
10
8
6
4
2
0 PPM
4.2
3.1
2.7
10.1
13.5
8.5
39.3

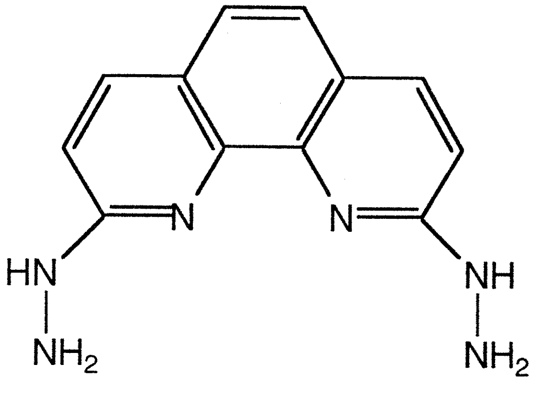
Figure 6: Dihydrazino ligands of pyridine, bipyridine, and phenanthroline.



2, 6 -dihydrazinopyridine



6, 6' -dihydrazino 2, 2' -bipyridine



2, 9 -dihydrazino 1, 10 -phenanthroline

CHAPTER 3

Technetium and Rhenium Organohydrazide Complexes from 2-Hydrazino-4(trifluoromethyl)pyrimidine

Introduction

The synthesis and characterization of rhenium and technetium diazenido complexes has been of interest for some time due to the importance of this chemistry to the radiopharmaceutical industry and to the elucidation of the chemistry of transition metal complexes with metal-nitrogen multiple bonds.[1-12] The reaction chemistry of chelating organohydrazines with rhenium and technetium metal centers has been explored recently.[13-18] The chelating organohydrazide complexes formed with rhenium and technetium are important since they are potential imaging agents that can be derivatized with proteins or other biologically relevant molecules in order to design them for uptake by specific biological systems. The reactivity of organohydrazines with the metal-oxo moiety of technetium makes them ideal for use in existing radiopharmaceutical kits containing technetium-oxo complexes.

Pyrimidine derivatives play an important role in biological systems and can be found in nucleic acids. Some metal complexes with hydrazine derivatives of pyrimidines have been synthesized with particular emphasis on the late transition metals cobalt,[19] nickel,[20,21] platinum,[22] copper,[23] zinc[24] and mercury.[21] These metal complexes have been synthesized in order to study the role of the metal ions in some biological systems and do not display redox chemistry during organohydrazide complexation with the metal. In contrast, the chemistry of hydrazinopyrimidine derivatives with the Group VII metals is expected to display redox chemistry to form metal-organohydrazide complexes. In particular, the synthesis and characterization of complexes of rhenium and technetium with the organohydrazine 2-hydrazino-4(trifluoromethyl)pyrimidine is described here. The complexes display the organohydrazide in three ligand forms, the terminal diazenido (1-) ligand (A), the chelating diazenido(1-) ligand (B) and the α-nitrogen protonated neutral, organodiazene ligand (C), as shown in Figure 1.

Experimental

Caution! ^{99}Technetium is a weak β-emitter (E = 0.292 MeV, $t_{1/2} = 2.12 \times 10^5$ years). All work has been done in laboratories approved for the use of low levels of radioactive materials. Precautions have been detailed elsewhere.[25]

Ammonium pertechnetate was supplied as a gift from DuPont Biomedical Products. Reagents and solvents were used as received unless otherwise specified. ^{1}H NMR spectra were recorded on a Varian XL-300 or Varian Unity-300 FTNMR spectrometer. The chemical shifts are referenced to the residual proton impurity in the deuterated solvent. Fast atom bombardment mass spectra of samples dissolved in *p*-nitrobenzylalcohol matrix were recorded with a Finnigan MAT 8200 mass spectrometer equipped with an Ion TechFAB gun operating at an accelerated voltage of 8 kV. The FAB gun produced a beam of 6-8 keV xenon neutrals. Elemental analyses were performed by Atlantic Microlab, Norcross, GA.

Syntheses. The complexes $ReO(PPh_3)_2Cl_3$,[26] $Tc(MeCN)(PPh_3)_2Cl_3$[27] and $Tc(NO)(MeCN)(PPh_3)_2Cl_2$[28] were prepared by the literature methods.

Preparation of $Tc(NNC_4H_2N_2CF_3)(PPh_3)_2Cl_2$ (1). To 0.04652 g (0.06325 mmol) of $Tc(MeCN)(PPh_3)_2Cl_3$ in a 100 mL rounded bottom flask equipped with a stir bar were added 10 mL of methanol and 0.02519 g (0.1414 mmol) of 2-hydrazino-4(trifluoromethyl)pyrimidine. An additional 15 mL of methanol was added, and the reaction was heated for 1.5 hours. At the end of this time, the solution was deep red, and a peach-tan colored solid had precipitated from the reaction solution. The solid was filtered on a fritted glass funnel, washed with methanol and dried *in vacuo*. The product was recrystallized from CH_2Cl_2/MeOH/Et_2O. Yield (0.0262 g, 50 %). Found: C, 56.0; H, 3.8; N, 6.4. $C_{41}H_{32}Cl_2F_3N_4P_2Tc$ requires C, 56.6; H, 3.7; N, 6.4; m/z 870 (M, 24 %); δ_H (ppm) (CD_2Cl_2) 7.95 (d); 7.6-7.4 (m); 7.4-7.2 (m); 6.4 (d).

Method 2: In a 50 mL rounded bottom flask with a stir bar, 0.5 mL NH_4TcO_4 (aq) (0.4187M) was evaporated to dryness. The pertechnetate was dissolved in 5 mL of methanol and 0.10533 g (0.59134 mmol) of 2-hydrazino-4(trifluoromethyl)pyrimidine was added along with an additional 10 mL of methanol. To the reaction mixture, 0.5 mL of a 0.48 M HCl methanolic solution was added. There was an immediate color change to deep red. The reaction was stirred at room temperature for 3 hours, and then it was evaporated to approximately 1 mL. To the deep-red solution, 0.13661 g (0.52083 mmol) PPh_3 was added, and the mixture was stirred for one hour at room temperature. The mixture was heated for two hours at reflux. A tan-peach solid precipitated out of solution. The reaction mixture was allowed to cool to room temperature; then it was filtered on a fritted glass funnel, washed with methanol and dried *in vacuo*. The product obtained from this method is spectroscopically identical to that obtained by method 1. X-ray quality crystals were obtained by recrystallization from CH_2Cl_2, methanol and diethyl ether. Yield (0.0289 g, 16 %).

Preparation of $Re(NNC_4H_2N_2CF_3)(PPh_3)_2Cl_2$ (2). To a 100 mL rounded bottom flask with a stir bar containing 0.0973 g (0.117 mmol) $ReO(PPh_3)_2Cl_3$ and 15 mL of methanol were added 0.0461 g (0.259 mmol) of 2-hydrazino-4(trifluoromethyl)pyrimidine. The reaction mixture was heated overnight. The solution was a deep red with a pink precipitate. The reaction mixture was filtered on a fritted glass funnel, washed with methanol and dried *in vacuo*. The product is formed in very low yield (< 5%). The amount isolated is enough to obtain a ^1H NMR spectrum and a mass spectrum. m/z 956 (M, 12 %); δ_H (ppm) (CD_2Cl_2) 7.52-7.42 (m); 7.4-7.2 (m); 6.26 (d); Note: The integration of the multiplet at 7.4 to 7.2 ppm indicates an additional proton, which can be attributed to a proton resonance from the pyrimidine ring.

Preparation of $Re(NNC_4H_2N_2CF_3)(HNNC_4H_2N_2CF_3)(PPh_3)Cl_2$ (3). To a 100 mL rounded bottom flask with a stir bar containing 0.0640 g (0.234 mmol) $NaReO_4$ and 5 mL of methanol was added 0.1264 g (0.7096 mmol) of 2-hydrazino-4(trifluoromethyl)pyrimidine. An additional 10 mL of methanol and 1 mL of a 0.48 M HCl/methanol solution. As the acid was added to the reaction mixture, the solution darkened. The reaction mixture was heated at reflux for one hour. After cooling to room temperature, the solvent was removed *in vacuo*, and the resulting dark red solid was redissolved in 1.5 mL of methanol. To the flask, 0.1632 g (0.6222 mmol) PPh_3 and 15 mL of methanol were added. The reaction mixture was heated overnight. A red precipitate formed, which was filtered on a fritted glass funnel, washed with methanol and dried *in vacuo*. X-ray quality crystals were obtained by recrystallization from CH_2Cl_2, methanol and diethyl ether. Yield (0.096 g, 47 %). Found: C, 39.7; H, 2.5; N: 12.3. $C_{28}H_{20}Cl_2F_6N_8PRe \bullet 1/2Et_2O$ requires C, 39.0; H, 2.5; N, 12.55; m/z 871 (M, 23%), 835 (M-Cl, 100); δ_H (ppm) (CD_2Cl_2) 18.1 (br); 9.3 (d); 8.95 (d); 7.5-7.2 (m); 6.95 (d). Note: Integration of the multiplet indicates the presence of an additional proton, which can be attributed to a proton resonance from the pyrimidine ring.

Preparation of a mixture of (2) and (3). To a 100 mL rounded bottom flask equipped with a stir bar, 0.5641 g (0.6771 mmol) $ReO(PPh_3)_2Cl_3$ and 10 mL methanol were added. To the mixture, 0.3837 g (2.154 mmol) 2-hydrazino-4(trifluoromethyl)pyrimidine and 10 mL methanol were added. One milliliter of a 0.48 M methanolic HCl solution was added. The reaction mixture was heated for 1.5 hours at which time a precipitate was observed. The reaction mixture was allowed to cool to room temperature, and it was filtered. The dark rose colored solid was washed with methanol and dried *in vacuo* to yield 0.1697 g of solid. The solid was identified to be a mixture of **(2)** and **(3)** by mass spectroscopy and by ^{1}H NMR spectroscopy. m/z 956 (M **(2)**, 9 %), 871 (M **(3)**, 27).

Preparation of $Tc(NO)(NNC_4H_2N_2CF_3)(PPh_3)_2Cl$ (4). To a 50 mL rounded bottom flask equipped with a stir bar were added 0.069 g (0.39 mmol) 2-hydrazino-4(trifluoromethyl)pyrimidine and 15 mL dichloromethane. To the solution, 0.07891 g (0.1031 mmol) $Tc(NO)(MeCN)(PPh_3)_2Cl_2$ and 10 mL dichloromethane were added. The reaction mixture was heated for approximately two hours. After cooling to room temperature, the reaction mixture was filtered, leaving a bright orange solution. The solution was allowed to evaporate to dryness, and the residue was redissolved in approximately 1 mL dichloromethane. Approximately 45 mL n-pentane was added to the orange solution, and an orange solid precipitated. The solid was collected on a fritted glass funnel, washed with n-pentane and dried *in vacuo*. The solid was dissolved in Et_2O to remove the unreacted ligand. The ether solution was reduced in volume to 1 mL, and n-pentane was added to precipitate the orange product. Yield of **(4)** (0.031 g, 35%); ν_{max} (KBr)/cm^{-1} (N≡O) 1717 vs; δ_H (ppm) (CD_2Cl_2) 10.6-10.5 (d); 7.9-7.7 (m); 7.3 (d); m/z 866 (M, 6.5%), 688 (10, M-$NNC_4H_2N_2CF_3$), 604 (40).

X-Ray Crystallographic Data Collection Parameters.

The data for **(1)** and **(3)** were collected using a Siemens platform goniometer with a CCD detector using graphite-monochromated molybdenum Kα radiation (λ = 0.71073 Å). The data for **(1)**, $C_{41}H_{32}Cl_2F_3N_4P_2Tc$, M = 868.55, were collected using a red-brown, prismatic crystal having dimensions 0.10 x 0.08 x 0.08 mm. The crystal system was triclinic, a = 11.9193(3) Å, b = 12.7026(3) Å, c = 14.1335(3) Å and α = 109.9320(10)°, β = 94.1250(10)°, γ = 105.0490(10)°, leading to a cell volume V = 1912.14(8) $Å^3$ with Z = 2. The space group was found to be $P\bar{1}$ The absorption coefficient was 0.651 mm^{-1}, the extinction coefficient was 0.0015(3), the calculated density D_c = 1.509 g/cm^3 and F(000) = 880. The data were obtained at 183(2) K in the θ range 1.56 to 20.00° with limiting indices $-9 \leq h \leq 13$, $-13 \leq k \leq 14$, $-15 \leq l \leq 15$. Of the 5714 reflections collected, 3528 were independent (R_{int} = 0.0455). No absorption correction was applied. The structure was solved by direct methods (SHELXTL v.5.0, Sheldrick, G. M. and Siemens Industrial Automation, Inc., 1995). Full-matrix least squares refinement based upon F^2 with 3425 data, zero restraints, and 479 parameters converged with final residuals: R_1 = 0.0568, wR_2 = 0.1189 and GOF = 1.135 based upon $I > 2\sigma(I)$. All non-hydrogen atoms were refined anisotropically.

The data for **(3)**, $C_{28}H_{20}Cl_2F_6N_8PRe$, M = 870.59, were collected using a dark red-brown, prismatic crystal having dimensions 0.20 x 0.10 x 0.08 mm. The crystal system was monoclinic, a = 10.1292(2) Å, b = 14.92310(10) Å, c = 20.6924(4) Å and $\alpha = \gamma = 90°$, β = 92.4560(10)°, leading to a cell volume V = 3124.97(9) Å^3 with Z = 4. The space group was found to be $P2_1/c$. The absorption coefficient was 4.181 mm^{-1}, the extinction coefficient was 0.00014(11), the calculated density D_c = 1.850 g/cm^3 and F(000) = 1688. The data were obtained at 183(2) K in the θ range 1.68 to 23.28° with limiting indices $-11 \leq h \leq 11$, $-16 \leq k \leq 16$, $-14 \leq l \leq 22$. Of the 12536 reflections collected, 4472 were independent (R_{int} = 0.0871). No absorption correction was applied. The structure was solved by direct methods (SHELXTL v.5.0, Sheldrick, G. M. and Siemens Industrial Automation, Inc., 1995). Full-matrix least squares refinement based upon F^2 with 4467 data, zero restraints, and 444 parameters converged with final residuals: R_1 = 0.0604, wR_2 = 0.1094 and GOF = 1.272 based upon $I > 2\sigma(I)$. All non-hydrogen atoms were refined anisotropically with the exception of the fluorines of the chelated diazene, which displayed a site disorder. Two complete sets of fluorines were refined isotropically with 50% occupancy per set.

Results and Discussion

The organohydrazines can react with metal complexes to form metal-organohydrazide complexes. This article presents complexes that contain two general ligand forms: the uninegative diazenido and the neutral, α-nitrogen protonated diazene. The potentially chelating organohydrazine, 2-hydrazino-4(trifluoromethyl)pyrimidine, provides an additional coordination mode, as shown in Figure 1. The chelated organohydrazide ligands form an extended π-system with the metal, and the unique electronic characteristics of complexes **(1)**, **(2)** and **(3)** may be attributed to the formation of this system. Complexes **(1)**, **(2)** and **(3)** are d^4, octahedral complexes that do not show any contact shift in the ^1H NMR spectra. Complex **(4)** is d^6, octahedral, and no contact shift would be expected. All four complexes show sharp resonances in the 6 to 8 ppm range of their ^1H NMR spectra, which is where these resonances are expected to be found in diamagnetic complexes; however, complexes **(1)**, **(2)**, and **(3)** are assigned to the formal oxidation state of +3.

The reaction of pertechnetate or perrhenate with the hydrazinopyrimidine ligand in methanol leads to a deep red solution. The resulting product has not been isolated as a solid in either case; however, if triphenylphosphine is added to the reaction mixture, isolable products are formed. The reaction chemistry of the hydrazinopyrimidine ligand with rhenium and technetium shows some differences. When triphenylphosphine is added to the pertechnetate reaction mixture, **(1)**, which contains two *trans*-triphenylphosphines, one chelated unprotonated diazenido ligand and two chloride ligands, is formed. In contrast, the addition of triphenylphosphine to the perrhenate reaction mixture leads to the formation of **(3)**, which consists of one triphenylphosphine, one chelated protonated diazene ligand, one unprotonated diazenido ligand and two chloride ligands. If $ReO(PPh_3)_2Cl_3$ is used as the starting material, **(2)**, which is analogous to the technetium product, **(1)**, is formed in low yield. Interestingly, if this reaction is carried out in the presence of added HCl, a mixture of **(2)** and **(3)** is formed, as seen by mass spectral analysis and ^1H NMR spectroscopy. The reason for the difference in reactivity between rhenium and technetium is unknown, and this reactivity is different than what is observed for reactions of rhenium and technetium with 2-hydrazinopyridine.[18] In the reactions with 2-hydrazinopyridine, a complex containing one organohydrazide ligand of the uninegative, chelated diazenido form, $M(NNpy)(PPh_3)_2Cl_2$, can be isolated in moderate yield for both rhenium and technetium.

It is interesting to note that complexes containing organohydrazide ligands can be synthesized from metal synthons ranging from the formal oxidation state of +7 to +1 to form complexes in the formal oxidation state of +3, as is the case with **(1)** - **(3)** or +1, as is the case with **(4)**. The reaction of the organohydrazine with the acetonitrile complexes, $Tc(MeCN)(PPh_3)_2Cl_3$ and $Tc(NO)(MeCN)(PPh_3)_2Cl_2$, leads to complexes in the formal oxidation states of +3 and +1, respectively. The coordinated acetonitrile may be reduced in the process of oxidizing the organohydrazine to the organohydrazide ligand and seems to be necessary in order for the reaction with the formally +3 metal synthon to occur.[18]

The chelated, unprotonated diazenido ligands found in **(1)**, **(2)**, and **(4)** and the monodentate, unprotonated diazenido ligand found in **(3)** are all uninegative ligands which form a σ-bond and a π-bond with the metal center. This multiple bonding of the uninegative diazenido ligands is indicated by the X-ray structural determination of **(1)** in which the technetium-α-nitrogen bond length is 1.810(8) Å and by the X-ray structural determination of **(3)** in which the rhenium-α-nitrogen bond length is 1.756(9) Å. The chelating diazene found in **(3)** is protonated on the α-nitrogen, making the overall charge on this ligand form neutral. The metal-nitrogen bond length of 1.937(9) Å is longer than that found for the uninegative diazenido ligand forms, as expected. The ^1H NMR spectrum of **(3)** displays a broad resonance at 18.1 ppm that is assigned to the α-nitrogen proton of the chelated diazene ligand. In addition to the longer metal-nitrogen bond length of the diazene ligand, the diazene metal-nitrogen-nitrogen bond angle of 129.0(7)° is indicative of sp^2 hybridization of the α-nitrogen in contrast to the nearly linear diazenido metal-nitrogen-nitrogen bond angle of 173.2(8)°, which is indicative of sp hybridization of the α-nitrogen. The extended π-system formed with the metal by the chelating organohydrazide may explain the non-contact shifted ^1H NMR spectra observed for the formally +3 complexes **(1)** - **(3)**. In addition to the chelating organohydrazide ligand, **(4)** has a linear nitrosyl ligand, as indicated by the stretching frequency found in the IR spectrum at 1717 cm^{-1}. Complex **(4)** is the first example of a rhenium or technetium complex in the formal oxidation state of +1 containing the chelated, uninegative diazenido formed from hydrazinopyridine or hydrazinopyrimidine.

Three of the four organohydrazide ligand forms encountered in the complexes synthesized from hydrazinopyridine reactions[16-18] are found in the complexes synthesized from hydrazinopyrimidine. The neutral zwitterionic form seen for hydrazinopyridine has not been seen in the complexes formed from hydrazinopyrimidine.[16] A possible explanation for the absence of this ligand form is the presence of the trifluoromethyl substituent in the hydrazinopyrimidine used in these reactions. The trifluoromethyl substituent causes the nitrogens of the pyrimidine ring to be less basic than the nitrogens of an unsubstituted pyrimidine ring, and as a result, protonation at these sites does not occur.

Conclusion

The organohydrazine 2-hydrazino-4(trifluoromethyl)pyrimidine reacts with technetium(VII), rhenium(VII), rhenium(V), technetium(III), and technetium(I) synthons to form metal-organohydrazide complexes. The organohydrazine acts as to reduce the metal center, with the exception of the metal-acetonitrile synthons, and in the process, the organohydrazine is oxidized to an organohydrazide ligand form. In the case of the metal-acetonitrile synthons, the acetonitrile may be reduced to form the organohydrazide complex. The complexes derived from the higher oxidation state synthons are formally assigned as +3 while the complex synthesized from the technetium(I) acetonitrile complex is formally assigned to a +1 oxidation state. The d^4, octahedral M(III)-organohydrazide complexes have ^1H NMR spectra that are characteristic of diamagnetic complexes. This characteristic may be attributed to the π-system formed by the chelating organohydrazide with the metal center.

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Table 1: Crystallographic Data for **(1)** and **(3)**.

Complex	$C_{41}H_{32}Cl_2F_3N_4P_2Tc$	$C_{28}H_{20}Cl_2F_6N_8PRe$
Molecular weight	868.55	870.59
Wavelength	0.71073 Å, Mo Kα	0.71073 Å, Mo Kα
Temperature, K	183(2)	183(2)
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a, Å	11.9193(3)	10.1292(2)
b, Å	12.7026(3)	14.92310(10)
c, Å	14.1335(3)	20.6924(4)
α, °	109.9320(10)	90
β, °	94.1250(10)	92.4560(10)
γ, °	105.0490(10)	90
Volume, $Å^3$	1912.14(8)	3124.97(9)
Z	2	4
Density (calculated), g/cm^3	1.509	1.850
Absorption coefficient, mm^{-1}	0.651	4.181
F(000)	880	1688
Diffractometer	Siemens SMART/CCD	Siemens SMART/CCD
Scan Type	ω Scans	ω Scans
θ range for data collection (°)	1.56 to 20.00	1.68 to 23.28
Limiting Indicies	$-9 \leq h \leq 13$, $-13 \leq k \leq 14$, $-15 \leq l \leq 15$	$-11 \leq h \leq 11$, $-16 \leq k \leq 16$, $-14 \leq l \leq 22$
Reflections Collected	5714	12536
Unique data	3528	4472
Absorption Correction	none	none

Refinement Method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/ restraints/ parameters	3425/ 0/ 479	4467/ 0/ 444
Goodness of Fit on F^2	1.135	1.272
Final *R* indicies [$I>2\sigma(I)$]	*R1* = 0.0586	*R1* = 0.0604
	wR2 = 0.1189	*wR2* = 0.1094
R indices (all data)	*R1* = 0.0737	*R1* = 0.0807
	wR2 = 0.1471	*wR2* = 0.1250
Extinction Coefficient	0.0015(3)	0.00014(11)
Largest diff. peak and hole	0.513 and -0.367 eÅ^{-3}	1.262 and -0.964 eÅ^{-3}

Table 2: Atomic Coordinates (x 10^4) and Equivalent Isotropic Displacement Parameters (Å^2 x 10^3) for **(1)**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Tc(1)	2974(1)	10774(1)	1940(1)	19(1)
Cl(1)	4827(2)	10613(2)	1481(2)	27(1)
Cl(2)	1813(2)	9989(2)	266(2)	28(1)
P(1)	2457(2)	8758(2)	1939(2)	23(1)
P(2)	3520(2)	12727(2)	1805(2)	22(1)
F(1)	-2253(7)	11959(9)	3458(6)	117(4)
F(2)	-937(8)	12969(9)	4796(8)	141(5)
F(3)	-1769(7)	11197(9)	4449(6)	104(3)
N(1)	3182(6)	11399(6)	3321(6)	24(2)
N(2)	2574(7)	11713(7)	4004(6)	31(2)
N(3)	1338(6)	11027(6)	2432(5)	24(2)
N(4)	627(7)	11805(7)	4005(6)	33(2)
C(1)	273(8)	10833(8)	1902(7)	31(3)
C(2)	-630(9)	11128(9)	2407(9)	41(3)
C(3)	-391(10)	11638(9)	3438(8)	39(3)
C(4)	1443(8)	11511(8)	3469(7)	27(2)
C(11)	3410(8)	8513(8)	2878(7)	27(2)
C(12)	3068(10)	7528(8)	3140(8)	43(3)
C(13)	3835(11)	7353(9)	3824(8)	50(3)
C(14)	4941(10)	8142(10)	4228(7)	43(3)
C(15)	5295(9)	9106(9)	3977(7)	35(3)
C(16)	4518(8)	9300(9)	3318(7)	28(2)
C(21)	2354(7)	13430(8)	2125(7)	21(2)

C(22)	1405(9)	13179(9)	1358(8)	36(3)
C(23)	456(8)	13597(10)	1601(8)	43(3)
C(24)	450(9)	14269(9)	2591(9)	44(3)
C(25)	1366(9)	14498(8)	3350(8)	39(3)
C(26)	2314(8)	14082(8)	3122(7)	32(3)
C(30)	-1317(11)	11997(14)	4039(10)	60(4)
C(31)	1003(8)	8428(7)	2298(7)	27(2)
C(32)	15(8)	8102(8)	1553(8)	33(3)
C(33)	-1101(9)	8017(9)	1797(9)	47(3)
C(34)	-1250(10)	8235(10)	2794(10)	53(3)
C(35)	-280(11)	8568(10)	3552(8)	55(3)
C(36)	840(9)	8668(9)	3287(8)	41(3)
C(41)	4848(8)	13794(8)	2702(7)	25(2)
C(42)	5193(9)	14961(9)	2776(7)	37(3)
C(43)	6219(9)	15764(9)	3441(7)	39(3)
C(44)	6928(9)	15401(9)	4000(7)	41(3)
C(45)	6599(9)	14273(9)	3955(7)	39(3)
C(46)	5556(8)	13464(8)	3309(7)	31(3)
C(51)	2327(7)	7528(7)	751(7)	23(2)
C(52)	2897(7)	7707(8)	-38(7)	26(2)
C(53)	2820(9)	6744(10)	-938(7)	37(3)
C(54)	2200(9)	5630(10)	-1042(8)	40(3)
C(55)	1628(9)	5439(9)	-266(8)	38(3)
C(56)	1693(8)	6367(8)	613(8)	34(3)
C(61)	3767(7)	12794(8)	565(6)	23(2)
C(62)	3693(8)	13759(8)	315(7)	29(2)
C(63)	3951(8)	13826(8)	-607(7)	28(2)

C(64)	4256(8)	12927(9)	-1312(7)	33(3)
C(65)	4299(8)	11964(9)	-1093(7)	33(3)
C(66)	4068(7)	11901(8)	-166(7)	23(2)

Table 3: Atomic Coordinates (x 10^4) and Equivalent Isotropic Displacement Parameters (Å^2 x 10^3) for **(3)**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Re(1)	2476(1)	6828(1)	3488(1)	21(1)
Cl(4)	4227(3)	6463(2)	2804(1)	29(1)
Cl(1)	4008(3)	6435(2)	4372(2)	38(1)
P(1)	1442(3)	7215(2)	2430(1)	21(1)
N(8)	-625(9)	6056(6)	4267(5)	28(2)
N(7)	-735(10)	4448(6)	4244(5)	32(2)
N(3)	3251(8)	8150(6)	3637(4)	24(2)
N(6)	862(9)	5160(6)	3691(5)	29(2)
N(5)	1519(9)	5856(6)	3565(4)	21(2)
N(2)	1276(9)	8359(6)	4152(5)	34(3)
N(1)	1222(9)	7510(6)	3970(5)	29(2)
C(2)	4811(12)	9344(9)	3664(6)	43(4)
C(8)	-2302(12)	5278(8)	4822(6)	36(3)
C(9)	-1676(11)	6063(8)	4644(5)	27(3)
C(7)	-1784(12)	4494(8)	4611(6)	32(3)
C(6)	-240(11)	5249(7)	4082(5)	23(3)
C(16)	1400(11)	6317(7)	1831(5)	24(3)
C(11)	1058(13)	6520(8)	1188(6)	37(3)
C(12)	985(13)	5848(10)	736(6)	45(4)
C(13)	1181(14)	4969(9)	913(6)	44(3)
C(14)	1463(13)	4747(8)	1542(7)	42(4)
C(15)	1590(11)	5421(7)	2004(6)	28(3)
C(26)	-282(10)	7554(7)	2420(5)	23(3)

C(21)	-798(11)	8161(8)	1970(6)	35(3)
C(22)	-2148(12)	8336(7)	1912(5)	30(3)
C(23)	-2994(12)	7879(8)	2312(6)	34(3)
C(24)	-2484(12)	7279(8)	2768(6)	33(3)
C(25)	-1138(10)	7114(7)	2819(6)	26(3)
C(36)	2317(10)	8150(8)	2088(6)	28(3)
C(31)	3312(10)	8034(9)	1656(6)	34(3)
C(32)	4055(13)	8733(11)	1440(7)	50(4)
C(35)	2105(13)	9014(8)	2309(6)	36(3)
C(3)	3896(12)	9855(8)	3987(6)	33(3)
C(10)	-2125(12)	6981(9)	4837(7)	40(3)
F(102)	-3038(8)	6952(5)	5270(4)	62(2)
F(101)	-1131(9)	7429(6)	5104(5)	78(3)
F(103)	-2568(12)	7464(6)	4354(4)	85(3)
C(4)	4238(22)	10795(11)	4184(9)	65(5)
F(42)	3568(68)	10963(31)	4728(27)	99(16)
F(41)	3803(73)	11462(42)	3753(31)	105(17)
F(43)	5460(30)	10952(33)	4272(45)	142(28)
N(4)	2754(10)	9551(7)	4153(5)	38(3)
C(1)	2461(11)	8705(7)	3972(5)	24(3)
C(5)	4450(12)	8486(8)	3500(7)	40(3)
C(34)	2876(15)	9716(9)	2113(7)	52(4)
C(33)	3824(16)	9576(11)	1676(8)	59(5)
F(42')	5383(51)	11076(29)	4012(31)	186(30)
F(43')	4200(54)	10983(19)	4783(13)	68(11)
F(41')	3380(82)	11291(24)	3911(27)	127(20)

Table 4: Bond lengths in Å of (**1**).

Tc(1)-N(1)	1.810(8)
Tc(1)-N(3)	2.181(7)
Tc(1)-Cl(1)	2.385(2)
Tc(1)-Cl(2)	2.390(2)
Tc(1)-P(1)	2.473(3)
Tc(1)-P(2)	2.472(3)
P(1)-C(31)	1.825(10)
P(1)-C(51)	1.825(9)
P(1)-C(11)	1.844(9)
P(2)-C(61)	1.824(9)
P(2)-C(21)	1.842(8)
P(2)-C(41)	1.837(9)
F(1)-C(30)	1.317(13)
F(2)-C(30)	1.27(2)
F(3)-C(30)	1.349(14)
N(1)-N(2)	1.267(10)
N(2)-C(4)	1.413(11)
N(3)-C(1)	1.345(11)
N(3)-C(4)	1.364(11)
N(4)-C(4)	1.327(12)
N(4)-C(3)	1.330(12)
C(1)-C(2)	1.395(13)
C(2)-C(3)	1.351(14)
C(3)-C(30)	1.51(2)
C(11)-C(16)	1.379(12)

C(11)-C(12)	1.393(13)
C(12)-C(13)	1.395(14)
C(13)-C(14)	1.373(14)
C(14)-C(15)	1.361(13)
C(15)-C(16)	1.392(13)
C(21)-C(26)	1.382(12)
C(21)-C(22)	1.400(12)
C(22)-C(23)	1.386(13)
C(23)-C(24)	1.370(14)
C(24)-C(25)	1.371(14)
C(25)-C(26)	1.381(13)
C(31)-C(36)	1.365(13)
C(31)-C(32)	1.392(12)
C(32)-C(33)	1.384(13)
C(33)-C(34)	1.375(14)
C(34)-C(35)	1.39(2)
C(35)-C(36)	1.399(14)
C(41)-C(42)	1.397(12)
C(41)-C(46)	1.396(12)
C(42)-C(43)	1.397(13)
C(43)-C(44)	1.381(14)
C(44)-C(45)	1.362(13)
C(45)-C(46)	1.403(13)
C(51)-C(52)	1.401(12)
C(51)-C(56)	1.409(12)
C(52)-C(53)	1.409(13)
C(53)-C(54)	1.367(14)

C(54)-C(55)	1.390(14)
C(55)-C(56)	1.371(13)
C(61)-C(62)	1.408(12)
C(61)-C(66)	1.395(12)
C(62)-C(63)	1.387(12)
C(63)-C(64)	1.385(13)
C(64)-C(65)	1.372(13)
C(65)-C(66)	1.382(12)

Table 5: Bond Angles in degrees of (**1**).

N(1)-Tc(1)-N(3)	69.7(3)
N(1)-Tc(1)-Cl(1)	107.6(2)
N(3)-Tc(1)-Cl(1)	176.5(2)
N(1)-Tc(1)-Cl(2)	153.3(2)
N(3)-Tc(1)-Cl(2)	83.7(2)
Cl(1)-Tc(1)-Cl(2)	99.04(8)
N(1)-Tc(1)-P(1)	91.3(2)
N(3)-Tc(1)-P(1)	92.4(2)
Cl(1)-Tc(1)-P(1)	89.93(8)
Cl(2)-Tc(1)-P(1)	88.45(8)
N(1)-Tc(1)-P(2)	92.9(2)
N(3)-Tc(1)-P(2)	90.3(2)
Cl(1)-Tc(1)-P(2)	87.49(8)
Cl(2)-Tc(1)-P(2)	88.42(8)
P(1)-Tc(1)-P(2)	175.58(9)
C(31)-P(1)-C(51)	104.2(4)
C(31)-P(1)-C(11)	104.0(4)
C(51)-P(1)-C(11)	103.5(4)
C(31)-P(1)-Tc(1)	107.9(3)
C(51)-P(1)-Tc(1)	119.3(3)
C(11)-P(1)-Tc(1)	116.3(3)
C(61)-P(2)-C(21)	104.3(4)
C(61)-P(2)-C(41)	104.4(4)
C(21)-P(2)-C(41)	103.9(4)
C(61)-P(2)-Tc(1)	117.8(3)

C(21)-P(2)-Tc(1)	110.6(3)
C(41)-P(2)-Tc(1)	114.5(3)
N(2)-N(1)-Tc(1)	138.0(6)
N(1)-N(2)-C(4)	105.4(7)
C(1)-N(3)-C(4)	115.1(8)
C(1)-N(3)-Tc(1)	131.8(6)
C(4)-N(3)-Tc(1)	113.1(6)
C(4)-N(4)-C(3)	114.3(8)
N(3)-C(1)-C(2)	120.7(9)
C(3)-C(2)-C(1)	117.9(10)
N(4)-C(3)-C(2)	124.0(9)
N(4)-C(3)-C(30)	114.8(10)
C(2)-C(3)-C(30)	121.1(11)
N(4)-C(4)-N(3)	127.9(9)
N(4)-C(4)-N(2)	118.4(9)
N(3)-C(4)-N(2)	113.8(8)
C(16)-C(11)-C(12)	118.0(9)
C(16)-C(11)-P(1)	119.8(7)
C(12)-C(11)-P(1)	122.2(7)
C(13)-C(12)-C(11)	120.4(10)
C(14)-C(13)-C(12)	119.9(10)
C(15)-C(14)-C(13)	120.7(9)
C(14)-C(15)-C(16)	119.4(9)
C(11)-C(16)-C(15)	121.6(9)
C(26)-C(21)-C(22)	118.7(8)
C(26)-C(21)-P(2)	121.8(7)
C(22)-C(21)-P(2)	119.1(7)

C(23)-C(22)-C(21)	120.1(9)
C(24)-C(23)-C(22)	120.2(9)
C(25)-C(24)-C(23)	119.9(9)
C(24)-C(25)-C(26)	120.6(9)
C(25)-C(26)-C(21)	120.4(9)
F(2)-C(30)-F(1)	111.2(12)
F(2)-C(30)-F(3)	104.8(11)
F(1)-C(30)-F(3)	102.6(11)
F(2)-C(30)-C(3)	114.8(11)
F(1)-C(30)-C(3)	112.9(11)
F(3)-C(30)-C(3)	109.5(11)
C(36)-C(31)-C(32)	117.8(9)
C(36)-C(31)-P(1)	123.1(7)
C(32)-C(31)-P(1)	118.2(7)
C(31)-C(32)-C(33)	121.7(9)
C(34)-C(33)-C(32)	119.6(10)
C(33)-C(34)-C(35)	119.9(10)
C(34)-C(35)-C(36)	119.3(10)
C(31)-C(36)-C(35)	121.7(10)
C(42)-C(41)-C(46)	118.0(8)
C(42)-C(41)-P(2)	120.5(7)
C(46)-C(41)-P(2)	121.5(7)
C(41)-C(42)-C(43)	120.4(9)
C(44)-C(43)-C(42)	120.3(10)
C(45)-C(44)-C(43)	120.4(10)
C(44)-C(45)-C(46)	119.8(9)
C(41)-C(46)-C(45)	121.1(9)

C(52)-C(51)-C(56)	117.8(8)
C(52)-C(51)-P(1)	120.6(7)
C(56)-C(51)-P(1)	121.5(7)
C(51)-C(52)-C(53)	120.1(9)
C(54)-C(53)-C(52)	120.4(10)
C(53)-C(54)-C(55)	120.2(9)
C(54)-C(55)-C(56)	120.0(9)
C(55)-C(56)-C(51)	121.5(9)
C(62)-C(61)-C(66)	117.3(8)
C(62)-C(61)-P(2)	121.5(7)
C(66)-C(61)-P(2)	121.2(7)
C(63)-C(62)-C(61)	120.7(8)
C(64)-C(63)-C(62)	120.4(9)
C(65)-C(64)-C(63)	119.6(9)
C(66)-C(65)-C(64)	120.3(9)
C(65)-C(66)-C(61)	121.6(8)

Table 6: Bond lengths in Å of (**3**).

Re(1)-N(5)	1.756(9)
Re(1)-N(1)	1.937(9)
Re(1)-N(3)	2.140(9)
Re(1)-Cl(4)	2.379(3)
Re(1)-Cl(1)	2.420(3)
Re(1)-P(1)	2.455(3)
P(1)-C(36)	1.812(11)
P(1)-C(26)	1.818(11)
P(1)-C(16)	1.825(11)
N(8)-C(6)	1.327(14)
N(8)-C(9)	1.346(13)
N(7)-C(7)	1.334(14)
N(7)-C(6)	1.344(13)
N(3)-C(5)	1.355(14)
N(3)-C(1)	1.363(13)
N(6)-N(5)	1.267(12)
N(6)-C(6)	1.414(13)
N(2)-N(1)	1.322(13)
N(2)-C(1)	1.372(14)
C(2)-C(5)	1.37(2)
C(2)-C(3)	1.39(2)
C(8)-C(7)	1.36(2)
C(8)-C(9)	1.39(2)
C(9)-C(10)	1.50(2)
C(16)-C(15)	1.39(2)

C(16)-C(11)	1.39(2)
C(11)-C(12)	1.37(2)
C(12)-C(13)	1.37(2)
C(13)-C(14)	1.36(2)
C(14)-C(15)	1.39(2)
C(26)-C(21)	1.39(2)
C(26)-C(25)	1.388(14)
C(21)-C(22)	1.39(2)
C(22)-C(23)	1.39(2)
C(23)-C(24)	1.38(2)
C(24)-C(25)	1.38(2)
C(36)-C(31)	1.39(2)
C(36)-C(35)	1.39(2)
C(31)-C(32)	1.37(2)
C(32)-C(33)	1.37(2)
C(35)-C(34)	1.38(2)
C(3)-N(4)	1.303(14)
C(3)-C(4)	1.50(2)
C(10)-F(103)	1.30(2)
C(10)-F(101)	1.31(2)
C(10)-F(102)	1.316(13)
C(4)-F(43)	1.26(3)
C(4)-F(43')	1.27(3)
C(4)-F(41')	1.26(6)
C(4)-F(42')	1.30(4)
C(4)-F(41)	1.39(7)
C(4)-F(42)	1.36(5)

F(42)-F(43')	0.65(4)
F(42)-F(41')	1.76(7)
F(41)-F(41')	0.61(7)
F(41)-F(42')	1.76(10)
F(43)-F(42')	0.57(10)
F(43)-F(43')	1.69(6)
N(4)-C(1)	1.347(14)
C(34)-C(33)	1.36(2)

Table 7: Bond Angles in degrees of (**3**).

N(5)-Re(1)-N(1)	90.6(4)
N(5)-Re(1)-N(3)	161.7(3)
N(1)-Re(1)-N(3)	71.8(3)
N(5)-Re(1)-Cl(4)	107.0(3)
N(1)-Re(1)-Cl(4)	161.6(3)
N(3)-Re(1)-Cl(4)	91.0(2)
N(5)-Re(1)-Cl(1)	94.0(3)
N(1)-Re(1)-Cl(1)	98.7(3)
N(3)-Re(1)-Cl(1)	84.0(2)
Cl(4)-Re(1)-Cl(1)	85.58(10)
N(5)-Re(1)-P(1)	93.4(3)
N(1)-Re(1)-P(1)	94.1(3)
N(3)-Re(1)-P(1)	93.0(2)
Cl(4)-Re(1)-P(1)	79.88(10)
Cl(1)-Re(1)-P(1)	165.09(9)
C(36)-P(1)-C(26)	105.5(5)
C(36)-P(1)-C(16)	107.3(5)
C(26)-P(1)-C(16)	101.7(5)
C(36)-P(1)-Re(1)	109.4(4)
C(26)-P(1)-Re(1)	116.6(4)
C(16)-P(1)-Re(1)	115.4(4)
C(6)-N(8)-C(9)	115.0(9)
C(7)-N(7)-C(6)	114.3(10)
C(5)-N(3)-C(1)	115.6(10)
C(5)-N(3)-Re(1)	129.7(8)

C(1)-N(3)-Re(1)	114.4(7)
N(5)-N(6)-C(6)	118.4(9)
N(6)-N(5)-Re(1)	173.2(8)
N(1)-N(2)-C(1)	108.0(9)
N(2)-N(1)-Re(1)	129.0(7)
C(5)-C(2)-C(3)	117.1(11)
C(7)-C(8)-C(9)	117.0(10)
N(8)-C(9)-C(8)	121.9(11)
N(8)-C(9)-C(10)	114.6(10)
C(8)-C(9)-C(10)	123.5(10)
N(7)-C(7)-C(8)	123.6(11)
N(8)-C(6)-N(7)	128.2(10)
N(8)-C(6)-N(6)	120.0(9)
N(7)-C(6)-N(6)	111.8(9)
C(15)-C(16)-C(11)	118.7(11)
C(15)-C(16)-P(1)	122.1(9)
C(11)-C(16)-P(1)	119.0(9)
C(12)-C(11)-C(16)	119.7(12)
C(11)-C(12)-C(13)	120.9(13)
C(14)-C(13)-C(12)	120.6(13)
C(13)-C(14)-C(15)	119.4(12)
C(14)-C(15)-C(16)	120.6(11)
C(21)-C(26)-C(25)	118.9(10)
C(21)-C(26)-P(1)	121.6(8)
C(25)-C(26)-P(1)	119.1(9)
C(26)-C(21)-C(22)	121.3(11)
C(21)-C(22)-C(23)	119.0(11)

C(24)-C(23)-C(22)	120.0(11)
C(25)-C(24)-C(23)	120.3(11)
C(24)-C(25)-C(26)	120.5(11)
C(31)-C(36)-C(35)	117.1(11)
C(31)-C(36)-P(1)	122.4(9)
C(35)-C(36)-P(1)	120.1(9)
C(32)-C(31)-C(36)	122.5(13)
C(31)-C(32)-C(33)	118.5(13)
C(34)-C(35)-C(36)	120.8(13)
N(4)-C(3)-C(2)	123.6(11)
N(4)-C(3)-C(4)	116.8(13)
C(2)-C(3)-C(4)	119.6(13)
F(103)-C(10)-F(101)	106.0(12)
F(103)-C(10)-F(102)	108.3(11)
F(101)-C(10)-F(102)	106.3(11)
F(103)-C(10)-C(9)	113.6(11)
F(101)-C(10)-C(9)	110.0(11)
F(102)-C(10)-C(9)	112.4(10)
F(43)-C(4)-F(43')	84(4)
F(43)-C(4)-F(41')	128(3)
F(43')-C(4)-F(41')	105(3)
F(43)-C(4)-F(42')	26(5)
F(43')-C(4)-F(42')	105(3)
F(41')-C(4)-F(42')	107(3)
F(43)-C(4)-F(41)	104(4)
F(43')-C(4)-F(41)	116(3)
F(41')-C(4)-F(41)	26(4)

F(42')-C(4)-F(41)	82(4)
F(43)-C(4)-F(42)	111(4)
F(43')-C(4)-F(42)	28(2)
F(41')-C(4)-F(42)	85(3)
F(42')-C(4)-F(42)	131(3)
F(41)-C(4)-F(42)	104(4)
F(43)-C(4)-C(3)	115(3)
F(43')-C(4)-C(3)	117(2)
F(41')-C(4)-C(3)	106(2)
F(42')-C(4)-C(3)	115(2)
F(41)-C(4)-C(3)	116(3)
F(42)-C(4)-C(3)	106(2)
F(43')-F(42)-C(4)	68(6)
F(43')-F(42)-F(41')	103(7)
C(4)-F(42)-F(41')	45(3)
F(41')-F(41)-C(4)	64(10)
F(41')-F(41)-F(42')	111(10)
C(4)-F(41)-F(42')	47(3)
F(42')-F(43)-C(4)	80(6)
F(42')-F(43)-F(43')	120(8)
C(4)-F(43)-F(43')	48(2)
C(3)-N(4)-C(1)	116.1(10)
N(4)-C(1)-N(3)	125.8(10)
N(4)-C(1)-N(2)	117.6(10)
N(3)-C(1)-N(2)	116.7(9)
N(3)-C(5)-C(2)	121.8(11)
C(33)-C(34)-C(35)	120.2(14)

C(34)-C(33)-C(32)	120.8(12)
F(43)-F(42')-C(4)	74(5)
F(43)-F(42')-F(41)	119(7)
C(4)-F(42')-F(41)	52(2)
F(42)-F(43')-C(4)	84(6)
F(42)-F(43')-F(43)	131(7)
C(4)-F(43')-F(43)	48(2)
F(41)-F(41')-C(4)	90(10)
F(41)-F(41')-F(42)	126(10)
C(4)-F(41')-F(42)	50(2)

Table 8: Anisotropic displacement parameters ($\mathrm{\AA}^2 \times 10^3$) for **(1)**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[(ha^*)^2U_{11} + ... + 2hka^*b^*U_{12}]$.

	U11	U22	U33	U23	U13	U12
Tc(1)	19(1)	21(1)	17(1)	7(1)	1(1)	7(1)
Cl(1)	26(1)	30(1)	32(1)	15(1)	10(1)	13(1)
Cl(2)	26(1)	37(2)	20(1)	7(1)	2(1)	11(1)
P(1)	25(2)	23(2)	21(2)	9(1)	5(1)	5(1)
P(2)	23(1)	24(2)	22(1)	9(1)	3(1)	11(1)
F(1)	94(6)	232(11)	75(6)	57(6)	38(5)	127(7)
F(2)	91(7)	127(8)	135(8)	-51(7)	48(6)	47(6)
F(3)	76(6)	171(9)	100(6)	69(7)	60(5)	61(6)
N(1)	23(5)	24(5)	24(5)	10(4)	-4(4)	5(4)
N(2)	33(5)	40(5)	19(5)	11(4)	5(4)	6(4)
N(3)	29(5)	26(5)	12(5)	1(4)	6(4)	11(4)
N(4)	37(6)	46(6)	26(5)	16(4)	11(5)	23(5)
C(1)	33(7)	38(6)	20(6)	8(5)	0(5)	9(5)
C(2)	27(6)	57(8)	52(8)	24(6)	20(6)	21(6)
C(3)	46(8)	48(7)	32(7)	15(6)	24(6)	25(6)
C(4)	28(7)	22(6)	32(7)	13(5)	4(6)	7(5)
C(11)	31(7)	23(6)	24(6)	2(5)	0(5)	11(5)
C(12)	55(7)	23(6)	37(7)	9(5)	-4(6)	-4(5)
C(13)	86(10)	35(7)	38(7)	24(6)	-6(7)	21(7)
C(14)	47(8)	49(8)	22(6)	-2(6)	-16(6)	26(7)
C(15)	37(7)	31(7)	38(7)	10(6)	9(5)	12(5)
C(16)	35(7)	41(7)	23(6)	17(5)	12(5)	27(6)
C(21)	24(6)	30(6)	22(6)	15(5)	13(5)	20(5)

C(22)	40(7)	43(7)	34(6)	18(5)	7(6)	21(6)
C(23)	22(6)	61(8)	50(8)	18(7)	1(5)	24(6)
C(24)	36(7)	51(7)	53(8)	13(7)	8(6)	33(6)
C(25)	37(7)	36(7)	38(7)	2(5)	19(6)	15(6)
C(26)	25(6)	40(6)	27(7)	3(5)	1(5)	17(5)
C(30)	53(9)	100(12)	57(9)	42(9)	36(8)	46(8)
C(31)	37(6)	16(5)	22(6)	1(5)	-3(5)	8(5)
C(32)	25(6)	36(6)	33(6)	7(5)	9(5)	8(5)
C(33)	36(7)	45(7)	45(8)	3(6)	11(6)	7(6)
C(34)	32(7)	55(8)	70(10)	23(7)	19(7)	8(6)
C(35)	58(9)	68(9)	30(7)	16(6)	14(7)	4(7)
C(36)	43(7)	54(7)	24(7)	14(6)	6(5)	11(6)
C(41)	21(5)	27(6)	24(6)	8(5)	4(5)	4(5)
C(42)	39(7)	37(7)	38(7)	23(6)	-4(6)	7(6)
C(43)	50(7)	36(7)	32(6)	18(6)	4(6)	7(6)
C(44)	40(7)	36(8)	28(6)	-2(5)	-9(5)	2(6)
C(45)	37(7)	32(7)	39(7)	5(6)	-11(6)	11(6)
C(46)	25(6)	26(6)	38(6)	9(5)	-2(5)	6(5)
C(51)	21(5)	15(6)	28(6)	2(5)	-2(5)	6(5)
C(52)	12(5)	28(6)	30(6)	3(5)	3(5)	5(4)
C(53)	34(6)	41(7)	29(7)	3(6)	1(5)	13(6)
C(54)	37(7)	45(8)	33(7)	-5(6)	3(6)	33(6)
C(55)	39(7)	20(6)	44(7)	1(6)	-5(6)	7(5)
C(56)	38(7)	31(7)	37(7)	14(6)	5(5)	14(5)
C(61)	25(6)	20(6)	21(6)	5(5)	2(4)	10(5)
C(62)	38(6)	25(6)	24(6)	5(5)	10(5)	16(5)
C(63)	27(6)	25(6)	35(7)	20(5)	-2(5)	5(5)

C(64)	25(6)	51(7)	29(6)	21(6)	9(5)	12(5)
C(65)	37(6)	43(7)	36(7)	23(6)	20(5)	25(5)
C(66)	26(6)	32(6)	28(6)	21(5)	12(5)	19(5)

Table 9: Anisotropic displacement parameters ($Å^2 \times 10^3$) for **(3)**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[(ha^*)^2U_{11} + ... + 2hka^*b^*U_{12}]$.

	U11	**U22**	**U33**	**U23**	**U13**	**U12**
Re(1)	20(1)	21(1)	21(1)	1(1)	6(1)	-1(1)
Cl(4)	26(2)	31(2)	32(2)	2(1)	10(1)	3(1)
Cl(1)	33(2)	50(2)	32(2)	14(2)	1(1)	-5(2)
P(1)	21(2)	20(2)	22(2)	2(1)	4(1)	0(1)
N(8)	28(5)	33(6)	23(5)	1(5)	6(4)	-3(5)
N(7)	41(6)	26(6)	28(6)	-5(5)	4(5)	-9(5)
N(3)	24(5)	27(5)	21(5)	3(5)	0(4)	0(5)
N(6)	36(6)	27(6)	26(6)	-4(5)	8(5)	-2(5)
N(5)	30(5)	24(5)	9(5)	-2(4)	-8(4)	7(4)
N(2)	35(6)	21(6)	47(7)	-14(5)	14(5)	-5(4)
N(1)	20(5)	27(6)	40(6)	7(5)	8(5)	-2(4)
C(2)	29(7)	62(9)	39(8)	-16(7)	11(6)	-34(7)
C(8)	37(7)	51(9)	20(7)	-1(6)	16(6)	-13(6)
C(9)	24(6)	40(7)	16(6)	-3(6)	-2(5)	-9(6)
C(7)	40(7)	30(7)	27(7)	3(6)	10(6)	-6(6)
C(6)	38(7)	21(6)	11(6)	2(5)	7(5)	-6(5)
C(16)	28(6)	25(7)	20(6)	-2(5)	3(5)	1(5)
C(11)	54(8)	28(7)	28(7)	-1(6)	0(6)	0(6)
C(12)	51(9)	62(10)	20(7)	-6(7)	-4(6)	-2(7)
C(13)	59(9)	43(9)	28(8)	1(7)	0(7)	-5(7)
C(14)	62(9)	15(6)	50(9)	-3(6)	18(8)	-10(6)
C(15)	42(7)	22(7)	20(6)	0(5)	9(6)	-5(5)
C(26)	24(6)	21(6)	26(6)	-11(5)	3(5)	-2(5)

C(21)	28(7)	34(7)	43(8)	6(7)	7(6)	5(6)
C(22)	46(8)	24(7)	21(6)	6(5)	2(6)	7(5)
C(23)	26(7)	41(8)	34(7)	-5(6)	-3(6)	-1(6)
C(24)	29(7)	35(7)	37(8)	4(6)	12(6)	-4(6)
C(25)	20(6)	32(7)	26(7)	8(5)	4(5)	1(5)
C(36)	26(6)	25(6)	32(7)	11(6)	-5(5)	2(6)
C(31)	19(6)	49(8)	35(7)	14(7)	6(5)	-2(6)
C(32)	30(8)	73(11)	45(9)	17(9)	0(7)	-1(7)
C(35)	58(9)	25(7)	23(7)	0(6)	-9(6)	-6(6)
C(3)	36(7)	37(8)	26(7)	2(6)	-2(6)	-11(6)
C(10)	31(7)	47(9)	45(8)	-13(8)	16(7)	-11(7)
F(102)	63(5)	59(5)	68(6)	-12(5)	37(5)	-1(4)
F(101)	58(6)	54(6)	123(9)	-51(6)	10(6)	-2(5)
F(103)	142(10)	64(6)	51(6)	14(5)	21(6)	50(6)
C(4)	120(18)	19(9)	56(12)	12(9)	8(12)	2(10)
F(42)	79(31)	86(21)	135(32)	-83(22)	48(25)	-82(21)
F(41)	163(44)	41(28)	112(29)	47(21)	15(25)	-43(23)
F(43)	21(21)	72(25)	330(75)	-32(35)	-38(31)	-28(17)
N(4)	39(6)	32(6)	43(7)	-3(5)	6(5)	-5(5)
C(1)	32(7)	22(6)	17(6)	4(5)	1(5)	-7(5)
C(5)	35(7)	40(8)	48(8)	-13(7)	19(7)	-8(6)
C(34)	79(11)	24(8)	51(9)	13(7)	-21(9)	-22(7)
C(33)	70(11)	60(11)	48(10)	38(9)	3(8)	-29(9)
F(42')	223(54)	81(22)	270(44)	-104(26)	203(50)	-125(29)
F(43')	95(27)	56(11)	54(13)	-24(10)	13(14)	-74(16)
F(41')	272(60)	7(13)	98(30)	4(16)	-28(30)	-62(21)

Table 10: Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for (**1**).

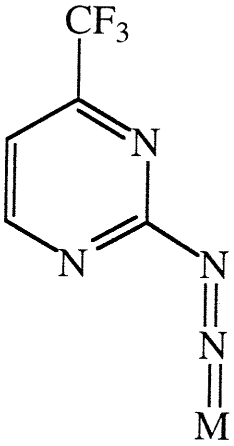
	x	y	z	U(eq)
H(1B)	134(8)	10491(8)	1176(7)	38
H(2B)	-1390(9)	10976(9)	2037(9)	50
H(12A)	2309(10)	6973(8)	2851(8)	51
H(13A)	3592(11)	6688(9)	4011(8)	60
H(14A)	5464(10)	8015(10)	4688(7)	51
H(15A)	6066(9)	9643(9)	4250(7)	42
H(16A)	4757(8)	9990(9)	3167(7)	34
H(22A)	1410(9)	12723(9)	669(8)	44
H(23A)	-192(8)	13416(10)	1080(8)	52
H(24A)	-189(9)	14577(9)	2752(9)	53
H(25A)	1348(9)	14947(8)	4038(8)	47
H(26A)	2942(8)	14244(8)	3655(7)	38
H(32A)	109(8)	7933(8)	860(8)	40
H(33A)	-1760(9)	7810(9)	1278(9)	56
H(34A)	-2016(10)	8158(10)	2963(10)	63
H(35A)	-376(11)	8726(10)	4243(8)	66
H(36A)	1505(9)	8909(9)	3809(8)	49
H(42A)	4728(9)	15211(9)	2372(7)	44
H(43A)	6430(9)	16564(9)	3508(7)	47
H(44A)	7649(9)	15941(9)	4418(7)	50
H(45A)	7074(9)	14034(9)	4360(7)	47
H(46A)	5327(8)	12680(8)	3285(7)	38
H(52A)	3336(7)	8478(8)	32(7)	31

H(53A)	3201(9)	6870(10)	-1475(7)	45
H(54A)	2161(9)	4985(10)	-1648(8)	48
H(55A)	1191(9)	4664(9)	-345(8)	46
H(56A)	1303(8)	6225(8)	1140(8)	41
H(62A)	3464(8)	14371(8)	784(7)	34
H(63A)	3918(8)	14492(8)	-758(7)	33
H(64A)	4434(8)	12977(9)	-1942(7)	40
H(65A)	4489(8)	11337(9)	-1581(7)	40
H(66A)	4116(7)	11234(8)	-22(7)	28

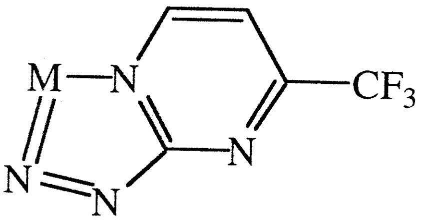
Table 11: Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for (**3**).

	x	y	z	U(eq)
H(1A)	518(9)	7213(6)	4084(5)	34
H(2A)	5648(12)	9579(9)	3561(6)	52
H(8A)	-3057(12)	5288(8)	5079(6)	43
H(7A)	-2192(12)	3950(8)	4733(6)	38
H(11A)	876(13)	7122(8)	1063(6)	44
H(12A)	797(13)	5992(10)	295(6)	53
H(13A)	1120(14)	4512(9)	594(6)	52
H(14A)	1572(13)	4137(8)	1663(7)	50
H(15A)	1807(11)	5270(7)	2441(6)	33
H(21A)	-219(11)	8464(8)	1694(6)	41
H(22A)	-2488(12)	8760(7)	1606(5)	36
H(23A)	-3920(12)	7979(8)	2271(6)	41
H(24A)	-3060(12)	6979(8)	3047(6)	40
H(25A)	-798(10)	6695(7)	3130(6)	31
H(31A)	3487(10)	7447(9)	1503(6)	41
H(32A)	4714(13)	8636(11)	1135(7)	59
H(35A)	1419(13)	9123(8)	2598(6)	43
H(5A)	5057(12)	8117(8)	3285(7)	48
H(34A)	2747(15)	10300(9)	2283(7)	63
H(33A)	4332(16)	10067(11)	1532(8)	71

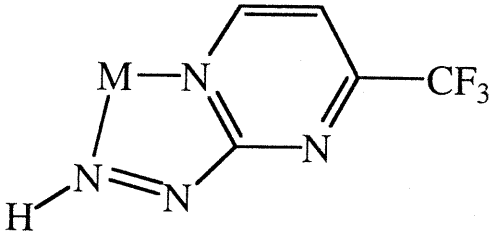
Figure 1: The terminal diazenido (1-) ligand (A); the chelating, diazenido (1-) ligand (B); and the neutral, organodiazene ligand (C).



A

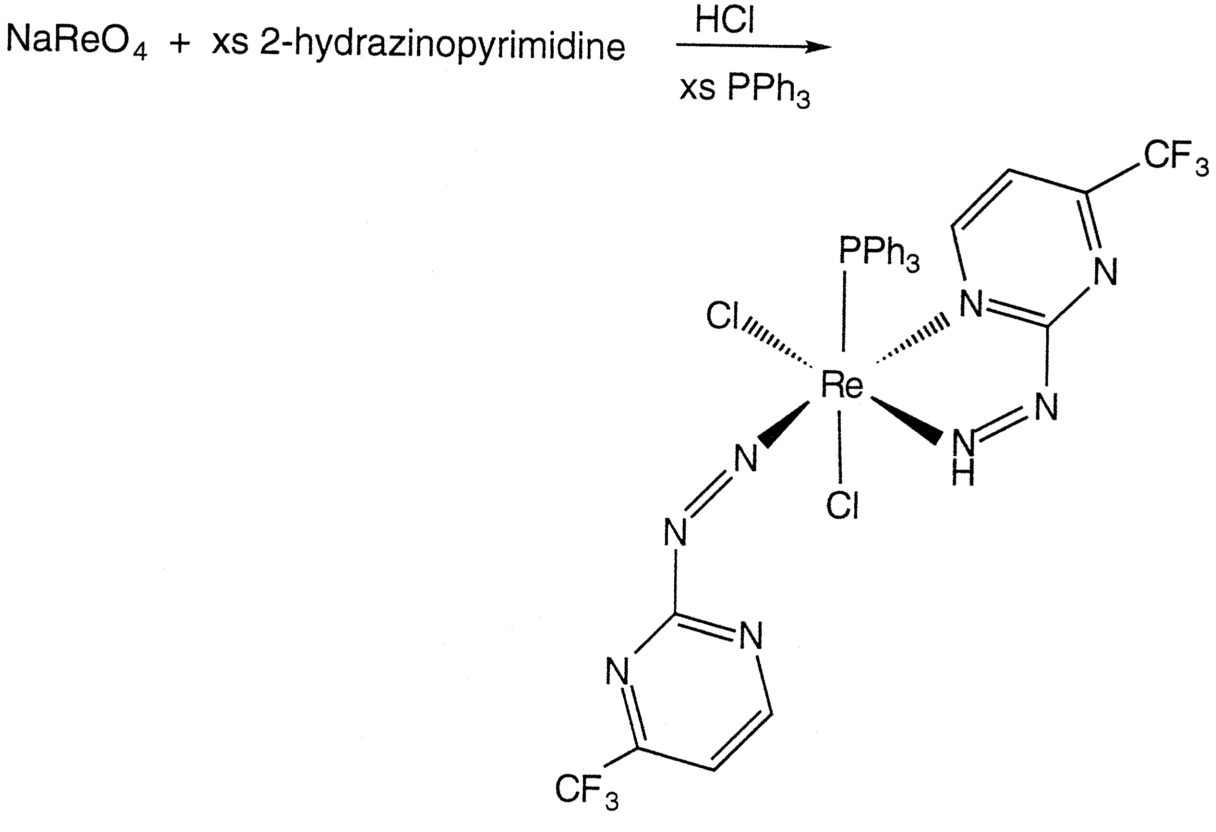


B

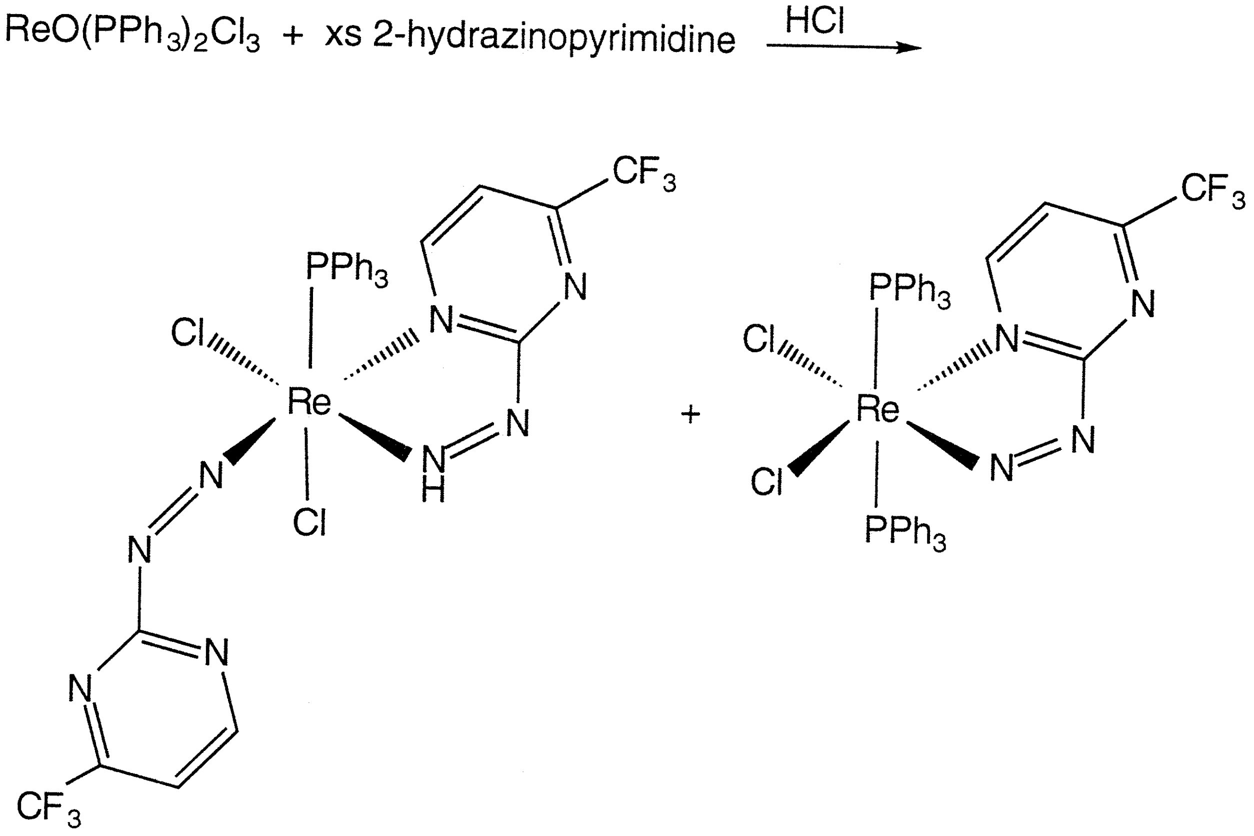


C

Reaction Scheme 1: Preparation of Re($NNC_4H_2N_2CF_3$)($NNC_4H_2N_2CF_3$)(PPh_3)Cl_2.


NaReO$_4$ + xs 2-hydrazinopyrimidine
HCl
xs PPh$_3$
CF$_3$
PPh$_3$
Cl
N
N
Re
N
N
NH
Cl
N
N
N
CF$_3$

Reaction Scheme 2: Preparation of a mixture of $Re(NNC_4H_2N_2CF_3)(HNNC_4H_2N_2CF_3)(PPh_3)Cl_2$ and $Re(NNC_4H_2N_2CF_3)(PPh_3)_2Cl_2$.


ReO(PPh3)2Cl3 + xs 2-hydrazinopyrimidine
HCl
CF3
PPh3
Cl
Re
N
N
N
N
H
Cl
N
N
N
N
CF3
+
CF3
PPh3
Cl
Re
N
N
N
N
Cl
PPh3

Reaction Scheme 3: Preparation of $Re(NNC_4H_2N_2CF_3)(PPh_3)_2Cl_2$.

$ReO(PPh_3)_2Cl_3$ + xs 2-hydrazinopyrimidine $\longrightarrow$

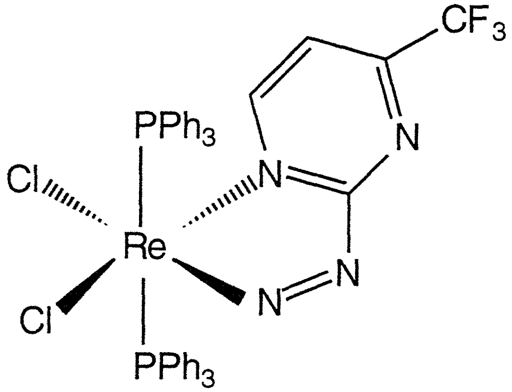


Figure 2: ORTEP of $Tc(NNC_4H_2N_2CF_3)(PPh_3)_2Cl_2$ with 35% ellipsoids.

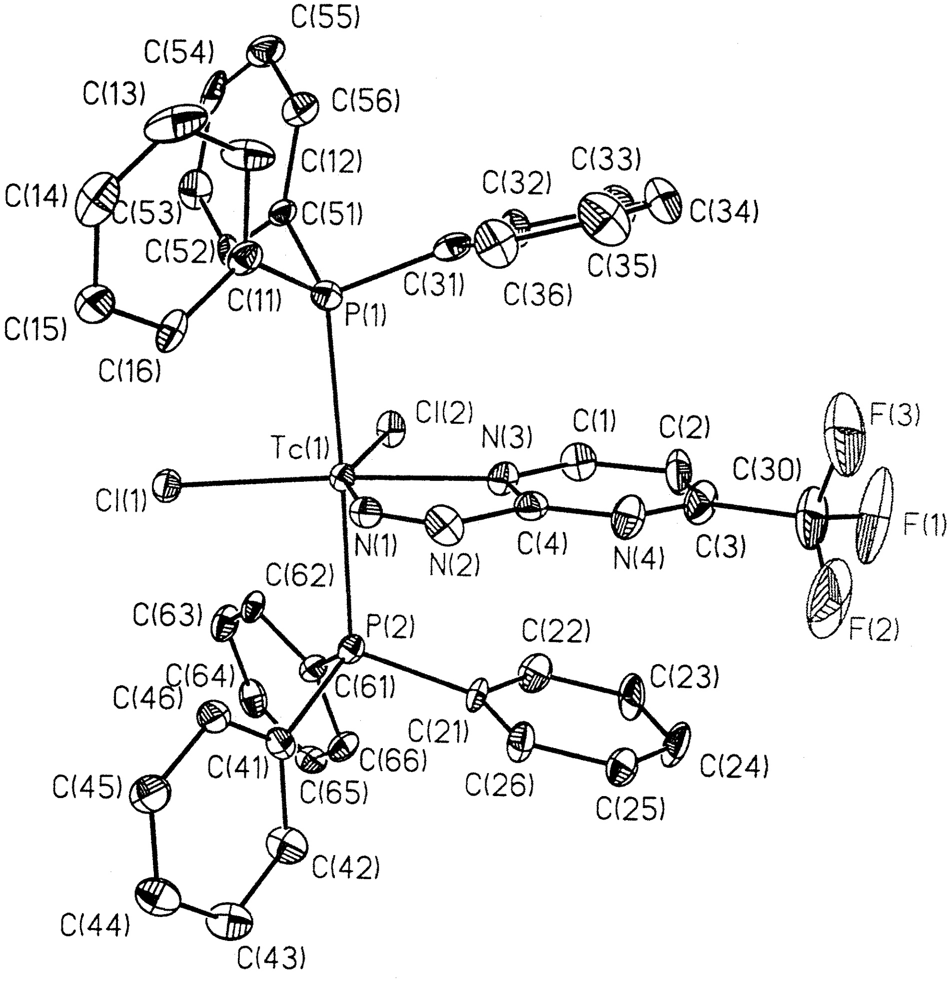

C(55)
C(54)
C(13)
C(56)
C(12)
C(33)
C(32)
C(14)
C(53)
C(51)
C(34)
C(52)
C(35)
C(11)
C(31)
C(36)
P(1)
C(15)
C(16)
Cl(2)
N(3)
C(1)
C(2)
F(3)
Tc(1)
C(30)
Cl(1)
F(1)
N(1)
N(2)
C(4)
N(4)
C(3)
C(62)
C(63)
P(2)
C(22)
F(2)
C(64)
C(61)
C(23)
C(46)
C(21)
C(66)
C(41)
C(45)
C(65)
C(24)
C(26)
C(25)
C(42)
C(44)
C(43)

Figure 3: PLUTO of $Re(NNC_4H_2N_2CF_3)(HNNC_4H_2N_2CF_3)(PPh_3)Cl_2$ including the hydrogen atoms. The fluorine atoms have been omitted for clarity.

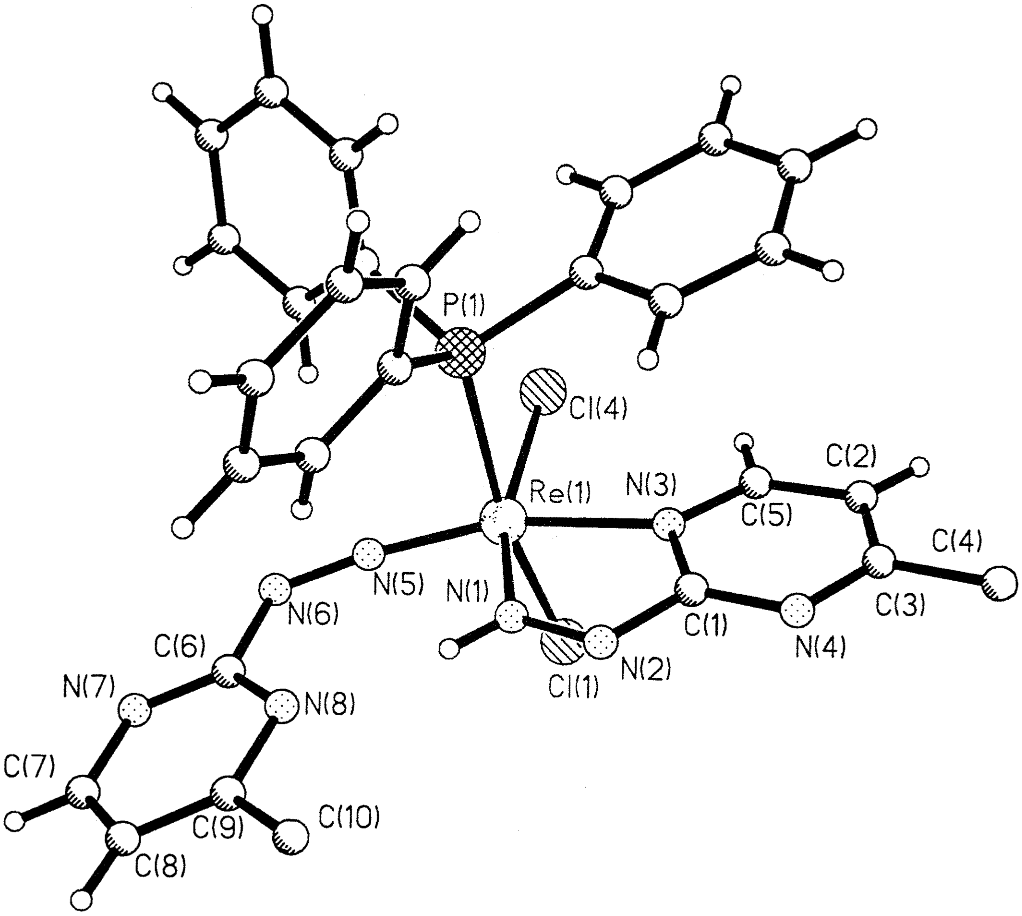
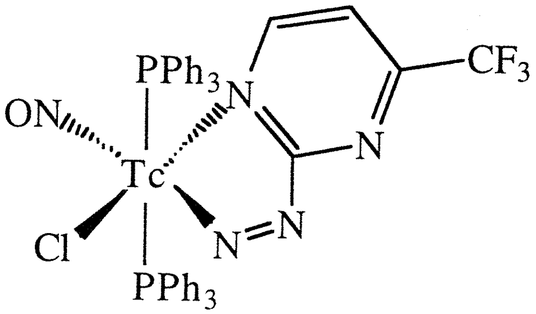

P(1)
Cl(4)
Re(1)
N(3)
C(5)
C(2)
C(4)
N(5)
N(1)
C(1)
C(3)
N(6)
N(4)
C(6)
Cl(1)
N(2)
N(7)
N(8)
C(7)
C(9)
C(10)
C(8)

Figure 4: Possible structural geometries of Tc(NO)($NNC_4H_2N_2CF_3$)(PPh_3)$_2$Cl.



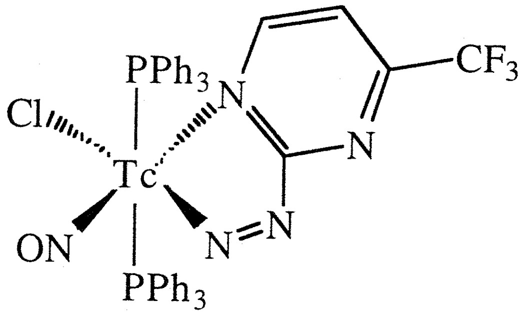


Figure 5: ^{1}H NMR Spectrum of $Tc(NNC_4H_2N_2CF_3)(PPh_3)_2Cl_2$.

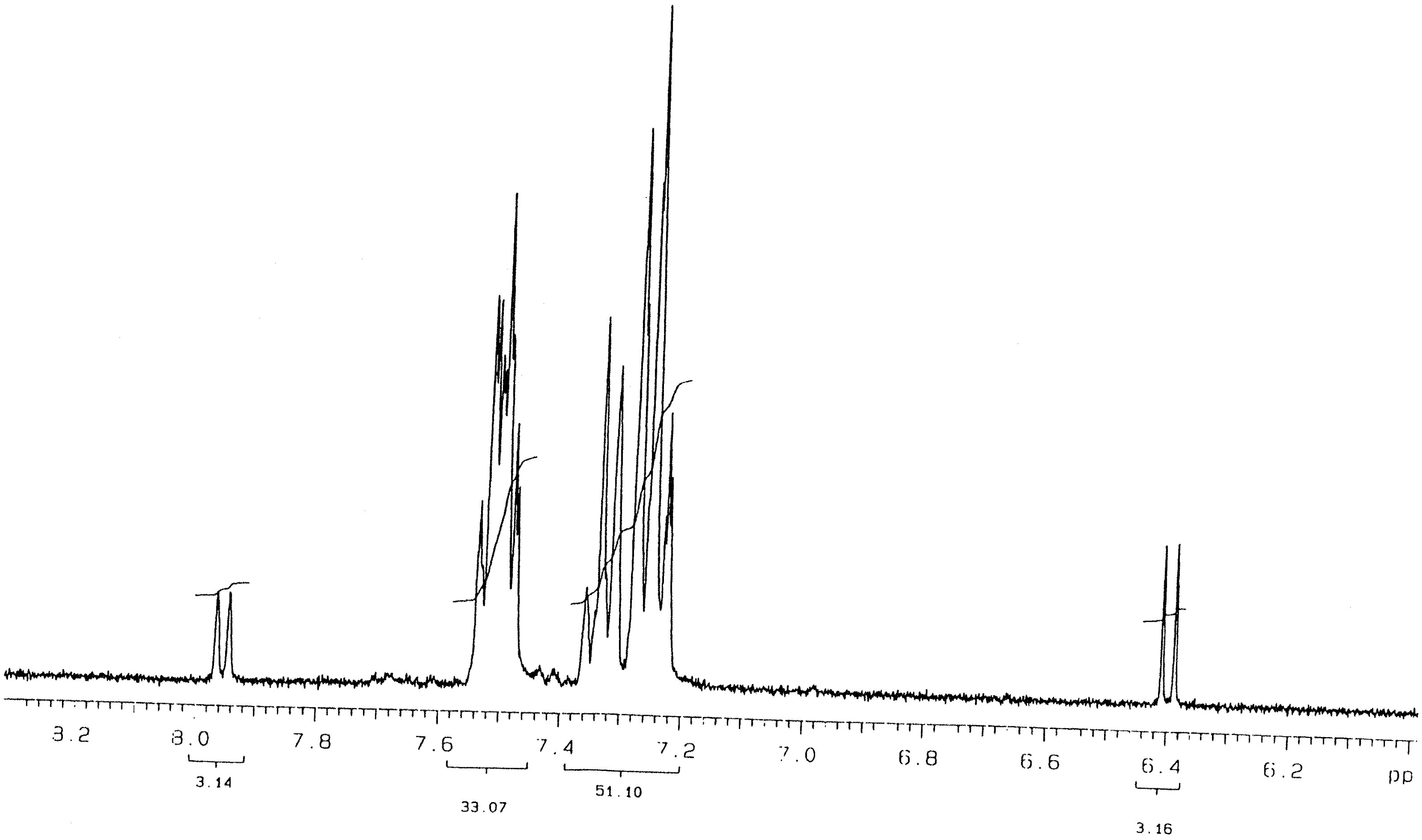

8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
pp
3.14
33.07
51.10
3.16

Figure 6: ^1H NMR Spectrum of $Re(NNC_4H_2N_2CF_3)(PPh_3)Cl_2$.

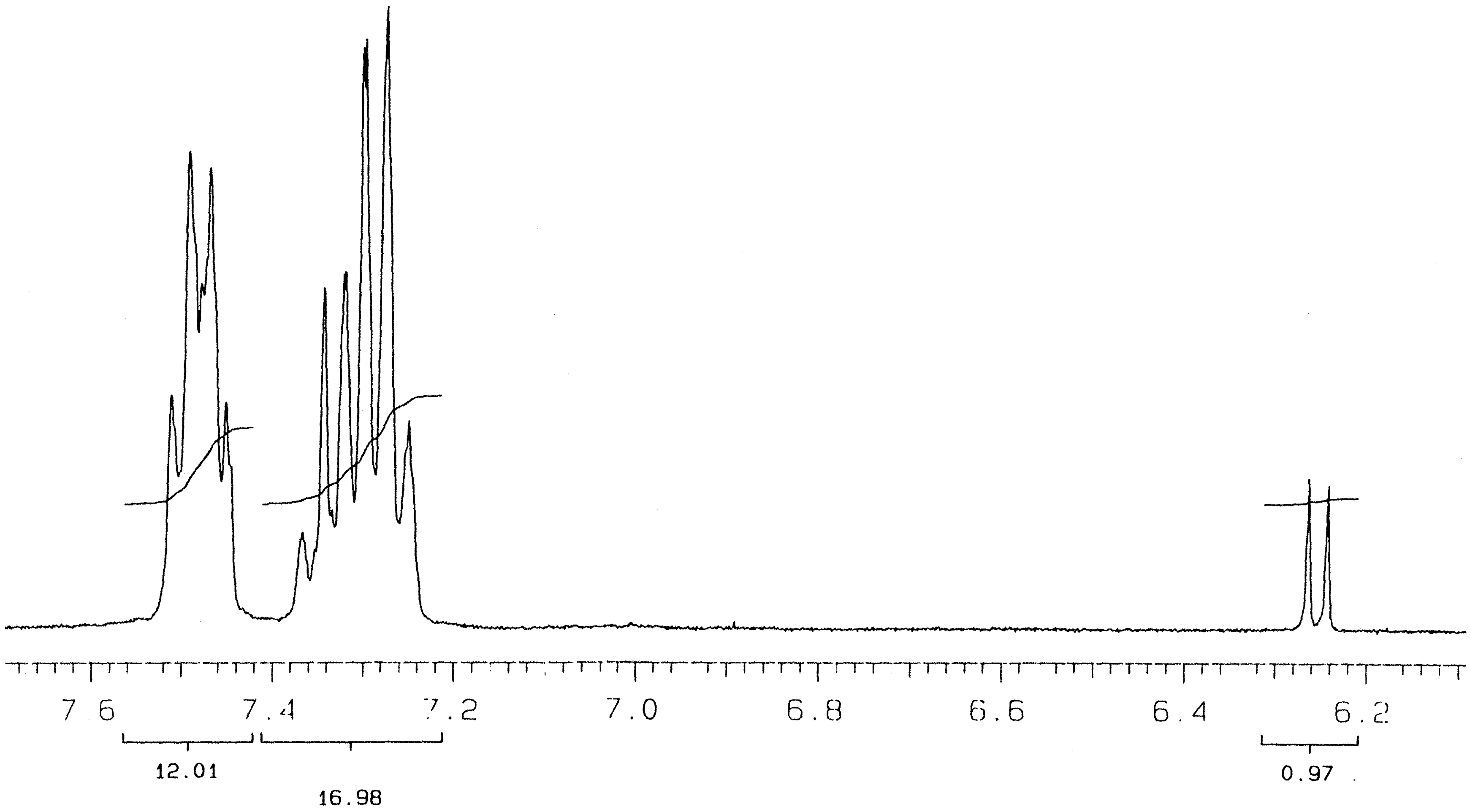

7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
12.01
16.98
0.97

Figure 7: ^{1}H NMR Spectrum of $Re(NNC_4H_2N_2CF_3)(HNNC_4H_2N_2CF_3)(PPh_3)Cl_2$. The α-nitrogen proton can be seen at 18.1 ppm.

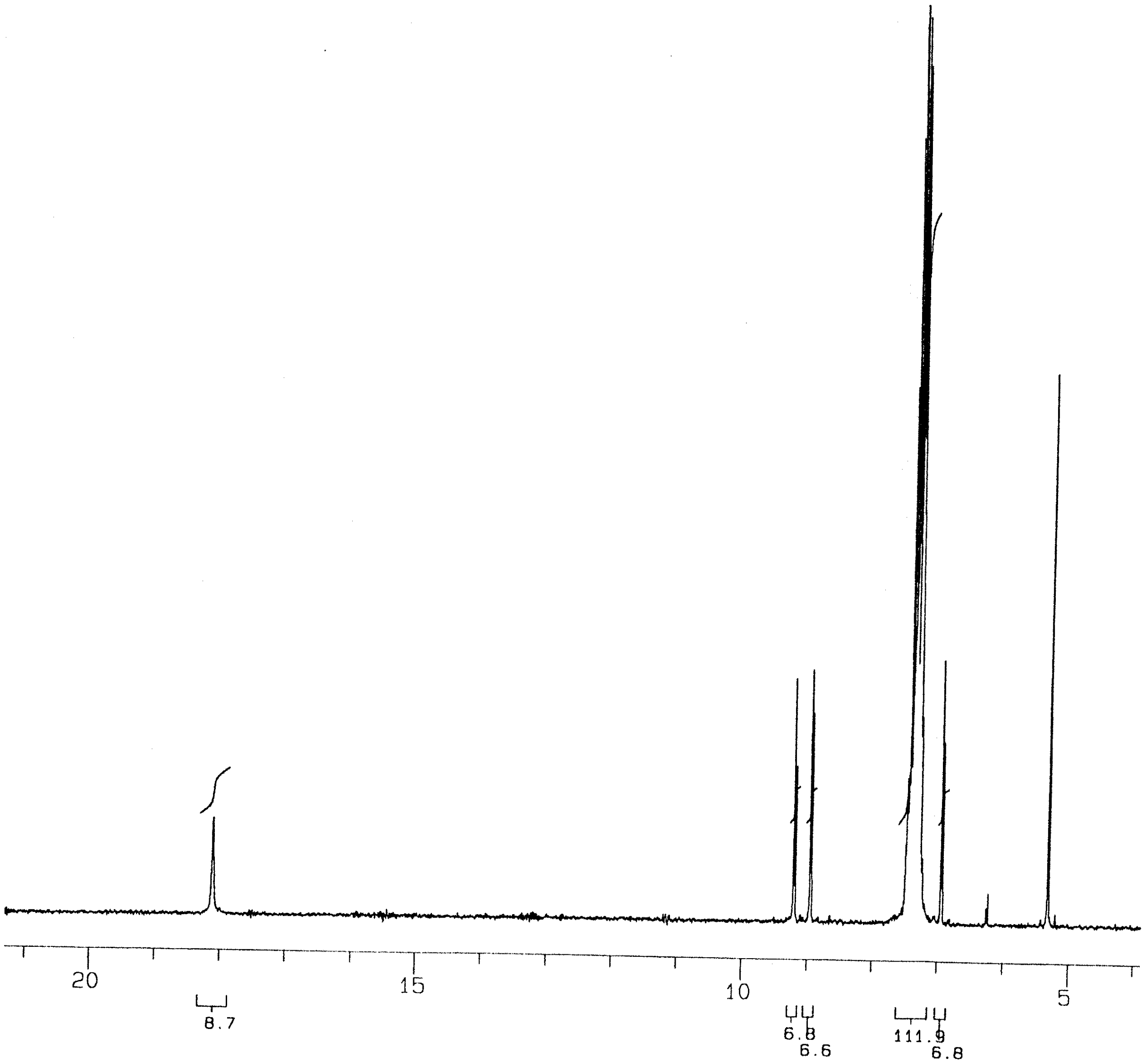
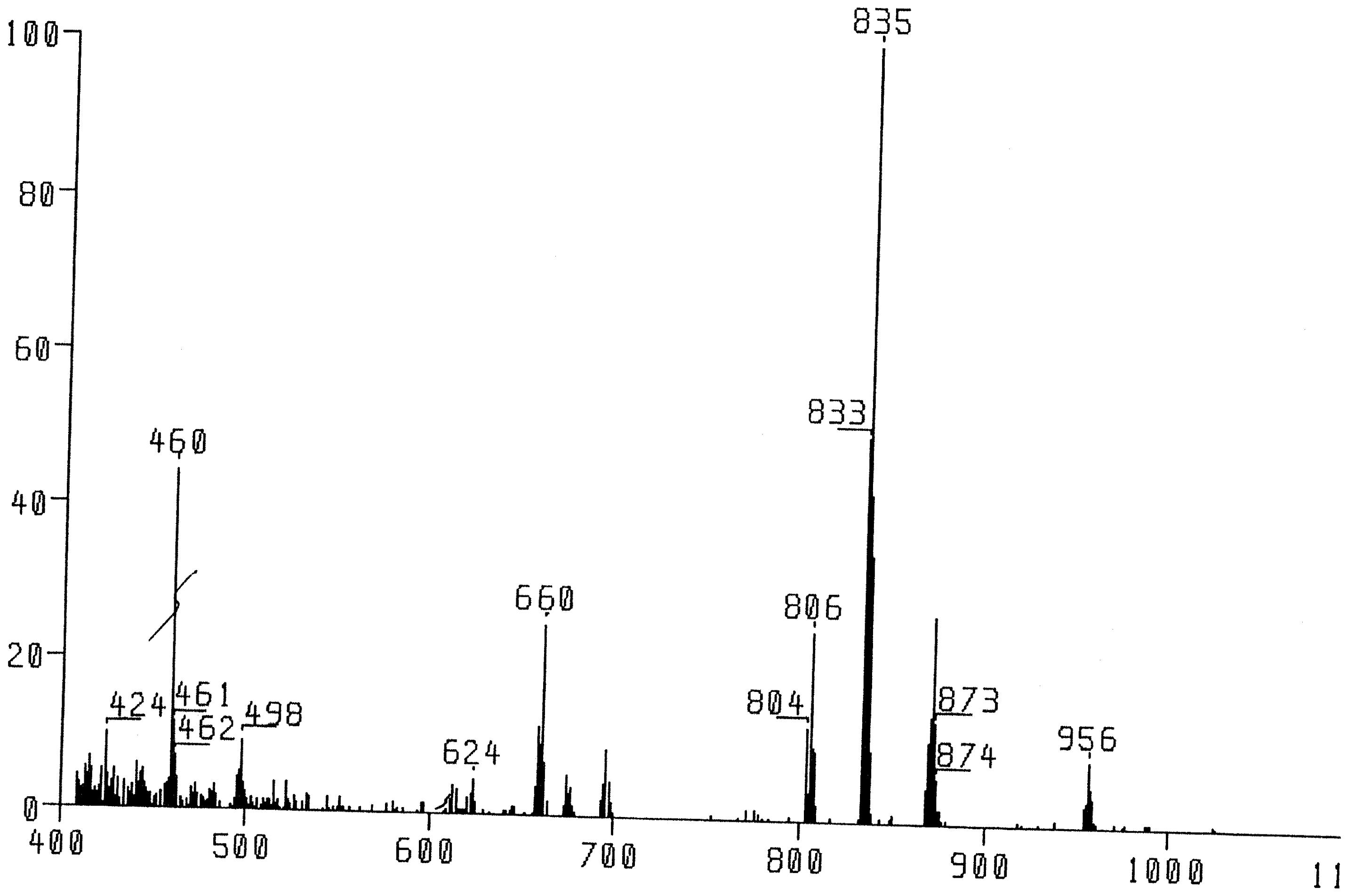

20
15
10
5
8.7
6.8
6.6
111.9
6.8

Figure 8: FAB(+) Mass Spectrum of a mixture of $Re(NNC_4H_2N_2CF_3)(HNNC_4H_2N_2CF_3)(PPh_3)Cl_2$ (871 m/z) and $Re(NNC_4H_2N_2CF_3)(PPh_3)_2Cl_2$ (956 m/z).


835
833
460
660
806
804
873
874
956
624
424
461
462
498
100
80
60
40
20
0
400
500
600
700
800
900
1000
11

CHAPTER 4

Synthesis and Characterization of Rhenium *cis*-Amide Complexes

Introduction

An interesting class of complexes is those involving a *cis*-amide bond to a rhenium metal center.[1,2] In these complexes, a four membered rhenium-oxygen-carbon-nitrogen ring is formed. There exist complexes which contain similar four-membered chelate rings such as rhenium dithiocarbamato complexes,[3] xanthate complexes,[4] and rhenium thiazetidine complexes.[5,6] There are also complexes that possess five-membered chelate rings that contain carbon, nitrogen, and oxygen.[7] These complexes form in shorter reaction times and with greater ease than the analogous four-membered *cis*-amide complexes. The goal of this research project is to synthesize and characterize a series of rhenium *cis*-amide complexes.

Experimental

Preparation of Re(CO)$_2$(PPh$_3$)$_2$(C$_5$H$_{10}$NCO) **(1)**. To a solution of 48.5 mg (0.429 mmol) ε-caprolactam in 9 mL THF under argon in a 50 mL round-bottomed flask with a sidearm in an ice/water bath was added with stirring 1.10 mL KN(TMS)$_2$ (0.5 M solution in toluene). The ice/water bath was removed after 10 minutes, and 334.5 mg (0.417 mmol) *trans*-Re(PPh$_3$)$_2$(CO)$_3$Cl[8] was added as a solid while stirring. After approximately one minute, an additional 8 mL THF was added. The flask was equipped with a condenser and was refluxed overnight. The lemon yellow reaction mixture was filtered through Celite545® (Fischer) on a fritted glass funnel (porosity D) twice. The filtrate was reduced in volume to about 1 mL *in vacuo*, and a sufficient amount of n-pentane (ca. 20 mL) was added to precipitate a light yellow solid. The solid **(1)** was filtered, washed with n-pentane, and dried; yield 153.7 mg (41.9%) of **(1)**. The solid was recrystallized three times from hot toluene, which was allowed to cool to room temperature, layered with n-pentane (1:5 by volume) yielding light yellow, X-ray quality crystals.

Anal. Calc. for $C_{44}H_{40}NO_3P_2Re$: C, 60.13; H, 4.59; N, 1.59. Found: C, 59.84; H, 4.71; N, 1.41.
IR(KBr): ν(C≡O) cm^{-1} 1921 (s), 1841 (s)
^{1}H NMR (CD$_2$Cl$_2$, 295 K) δ (ppm) 7.59-7.35 (m), 2.62-2.52 (broad), 1.20-0.90 (broad), 0.75-0.62 (broad), 0.34-0.22 (broad).
^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 295 K) δ (ppm) 29.3 (s)

Preparation of Re(CO)$_2$(PPh$_3$)$_2$(C$_4$H$_8$NCO) **(2)**. This complex was prepared according to the procedure for **(1)** using δ-valerolactam; yield 48.4% of **(2)**. The product was recrystallized giving light yellow microcrystals of **(2)**.

Anal. Calc. for $C_{43}H_{38}NO_3P_2Re$: C, 59.71; H, 4.43; N, 1.62. Found: C, 59.82; H, 4.41; N, 1.62.

IR(KBr): ν(C≡O) cm^{-1} 1916 (s), 1838 (s)

^1H NMR (CD_2Cl_2, 294 K) δ (ppm) 7.7-7.15 (m), 2.50 (broad), 0.95 (broad), 0.60 (broad).

$^{31}P\{^1H\}$ NMR (CD_2Cl_2, 294 K) δ (ppm) 31.0 (s)

Preparation of $Re(CO)_2(PPh_3)_2(C_5H_{10}NCS)$ **(3)**. This complex was prepared according to the procedure for **(1)** using ω-thiocaprolactam; yield 31.4% (crude) of **(3)** as a yellow powder.

IR(KBr): ν(C≡O) cm^{-1} 1905 (s), 1826 (s).

^1H NMR (CD_2Cl_2, 293 K) δ (ppm) 7.78-7.62 (m), 7.50-7.30 (m), 2.60-2.50 (broad), 1.34-1.25 (broad), 1.20-0.90 (broad), 0.80-0.70 (broad), 0.32-0.22 (broad).

$^{31}P\{^1H\}$ NMR (CD_2Cl_2, 293 K) δ (ppm) 26.2 (s).

Preparation of $HB(pz)_3Re(O)(NCOC_5H_{10})_2$ **(4)**. To a solution of 50.8 mg (0.450 mmol) of ε-caprolactam in 4 mL of THF in a 50 mL round-bottomed flask with a sidearm in an ice/water bath was added with stirring 1.00 mL $KN(TMS)_2$ (0.5 M solution in toluene). The reaction mixture was allowed to stir for ten minutes after which time the ice bath was removed. The solvent was evaporated to dryness *in vacuo*. An additional 4 mL of THF was added, and then 96.4 mg (0.201 mmol) $HB(pz)_3ReOCl_2$ as a solution in 4 mL of THF was added. The reaction mixture was allowed to react for a little over an hour when it seemed the color change from sky-blue to purple-red was complete. The solvent was evaporated to dryness *in vacuo*, and the solid was washed with Et_2O, filtered, and dissolved in acetone giving a purple solution. The acetone solution was placed in the freezer, where a purple solid formed.

IR(KBr): ν (Re≡O) cm^{-1} 908 (s).

^1H NMR (C_6D_6, 298 K) δ (ppm) 7.68 (s), 7.58 (s), 6.56-6.44 (broad), 6.18 (s), 3.60-3.54 (m), 2.42-2.34 (m), 2.28-2.20 (m), 1.32-1.20 (m), 1.20-1.10 (m), 1.10-0.98 (m).

Reactions of N-isopropylbenzamide, 2-pyrrolidinone, oxindole, and acetamide with *trans*-chlorobis(triphenylphosphine)tricarbonylrhenium(I) according to the procedure for **(1)** yielded a mixture of products that were seen using IR spectroscopy in the 2000 to 1800 cm^{-1} region.

X-Ray Crystallographic Data Collection Parameters.

A yellow prismatic crystal of **(1)** having dimensions of 0.280 x 0.280 x 0.360 mm was selected and mounted. All measurements were made on an Enraf-Nonius CAD-4 diffractometer with graphite monochomated Mo Kα radiation. The crystal system was triclinic, $a = 12.102(2)$ Å, $b = 13.981(2)$ Å, $c = 14.011(2)$ Å, and $\alpha = 97.57(3)^\circ$, $\beta = 112.51(3)^\circ$, $\gamma = 94.71(3)^\circ$, leading to a cell volume $V = 2148(2)$ Å^3 with $Z = 2$. The space group was found to be $P\bar{1}$. The absorption coefficient was 29.8 cm^{-1}, the calculated density $\rho = 1.501$ $\mathrm{g/cm}^3$, and F(000) = 980. The data were obtained at -86°C with 2θ equal to 49.9°. Of the 7936 reflections collected, 7542 were unique ($R_{int} = 0.086$). An empirical absorption correction was applied which resulted in transmission factors ranging from 0.79 to 1.49. The data were corrected for Lorentz polarization effects. The structure was solved by direct methods, and the non-hydrogen atoms were refined anisotropically. Least squares refinement was based on 6096 observed reflections ($I > 3.00\ \sigma(I)$) and 523 parameters converged with final residuals: $R_1 = 0.067$ and $R_w = 0.073$, and GOF = 2.43.

Results and Discussion

The reaction of $Re(CO)_3(PPh_3)_2Cl$ with one equivalent of potassium amide produces the rhenium *cis*-amide complexes **(1)**, **(2)**, and **(3)**, in good yields. All the complexes are air and temperature stable. The complexes were characterized by elemental analysis and ^1H NMR, ^{31}P NMR, and IR spectroscopies. From both the IR and ^{31}P NMR spectroscopies, the geometry of the complexes can be determined. The absorption bands for the carbonyls attached to the metal center are two strong bands of similar intensity, which are characteristic for the *cis*-geometry.[9] The resonances occur in the region of 1921-1816 cm^{-1}. The absorption band for the ligand carbonyl was not assigned because it has shifted to lower wavenumbers and cannot be discerned; however, the disappearance of the carbonyl stretch in the 1700-1600 cm^{-1} range indicates that the ligand has chelated to the metal instead of binding in a monodentate fashion. The ^{31}P NMR spectrum reveals a singlet in the range of 26 to 31 ppm. The singlet indicates that both phosphorus atoms are chemically equivalent. This condition can only be satisfied by placing the phosphorus atoms *trans* to each other. From these data, the structural geometry was determined and is confirmed by the X-ray crystal structure shown in Figure One.

The amides employed to form complexes **(1)**, **(2)**, and **(3)** are sterically unhindered because they are cyclic. Sterics is a factor in these reactions because when the reaction to form a *cis*-amide complex is attempted with a ligand that has bulky substituents on the nitrogen, such as the isopropyl group on N-isopropylbenzamide, the desired product does not form cleanly. Another factor in these reactions is the bite angle of the of the *cis*-amide. The amides used to form complexes **(1)**, **(2)**, and **(3)** are six- and seven-membered rings. These ligands complex to the metal to form one complex cleanly. When the same reaction is attempted with a five-membered lactam, 2-pyrrolidinone, the reaction does not form the desired *cis*-amide product in a reasonable yield. This factor probably is due to the additional ring strain encountered from the chelation of a five-membered ring ligand to a metal center. The five-membered ring is expected to have the largest oxygen-carbon-nitrogen angle of the five-, six-, and seven-membered cyclic amides used in these reactions. The five-membered ring angle may not be favorable for chelation to the metal center. In addition, the reaction between oxindole, a five-membered lactam fused to a benzene ring, and $Re(CO)_3(PPh_3)_2Cl$ does not yield any chelated *cis*-amide product.

Reaction of *trans*-$Re(PPh_3)_2(CO)_3Cl$ with acetamide did not yield a clean product. Instead, a dark yellow, sticky solid resulted from the reaction mixture. The IR region from 2000 to 1800 cm^{-1} displayed many bands, indicating the formation of many products. A significant difference between the six- and seven-membered cyclic amides and acetamide is the smaller size of acetamide. Trifluoroacetamide reacts more cleanly giving two singlets seen by ^{31}P NMR. One of these products is the η^1-amide, which displays a strong IR band at 1654 cm^{-1}. Trifluoroacetamide cannot be compared directly to acetamide because the fluorines make the electronics of the ligand completely different and the fluorines differ in size from the hydrogens significantly.

Attempts to make higher oxidation state rhenium *cis*-amide complexes have been unsuccessful. When ε-caprolactam was reacted with dichloro[hydrotris(1-pyrazolyl)borato]oxorhenium(V), two amide ligands complexed with the metal in a monodentate fashion to yield an air stable purple complex **(4)**. This mode of bonding is confirmed by the resonance present in the IR at 1648 cm^{-1}, which is assigned to the carbonyl stretch of the amide. The oxo is still present and shows a strong resonance at 908 cm^{-1}. Reaction of the potassium salt of ε-caprolactam and higher oxidation state rhenium-oxo complexes such as $ReO(PPh_3)_2Cl_3$ and $[TBA][ReOBr_4]$ (TBA = tetrabutylammonium) led to the formation of a dark solid that was insoluble in organic solvents.

There are two factors that may contribute to the differences in reactivity of amides versus the analogous four- and five-membered ligands mentioned previously in the introduction. The amide is a poor nucleophile due to the resonance stabilization from the lone pair of nitrogen through the orbitals of the carbonyl.[10] The lack of nucleophilicity of the amide does not allow for its ready substitution to a metal center and may explain the need for harsher reaction conditions of the amide versus some similar ligands that are in the literature.

Conclusion

A series of rhenium(I) *cis*-amide complexes have been synthesized. These complexes do not form as readily as some of the related four- and five-membered chelate complexes of rhenium. This feature is a result of the electronic nature of a *cis*-amide. The amides employed vary in size and in electronic properties, and not all the amides form a chelate complex with rhenium. A rhenium(V)-oxo bis(amide) complex was synthesized in which the amides are bound through the nitrogens to the metal center.

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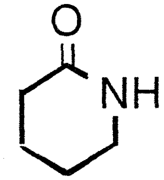
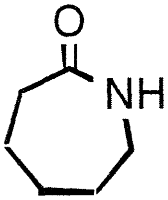
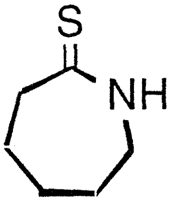
Figure 1: *cis*-Amide and Thioamide Ligands.



δ-Valerolactam



ε-Caprolactam



ω-Thiocaprolactam

Figure 2: Preparation of *cis*-Amide and Thioamide Complexes.

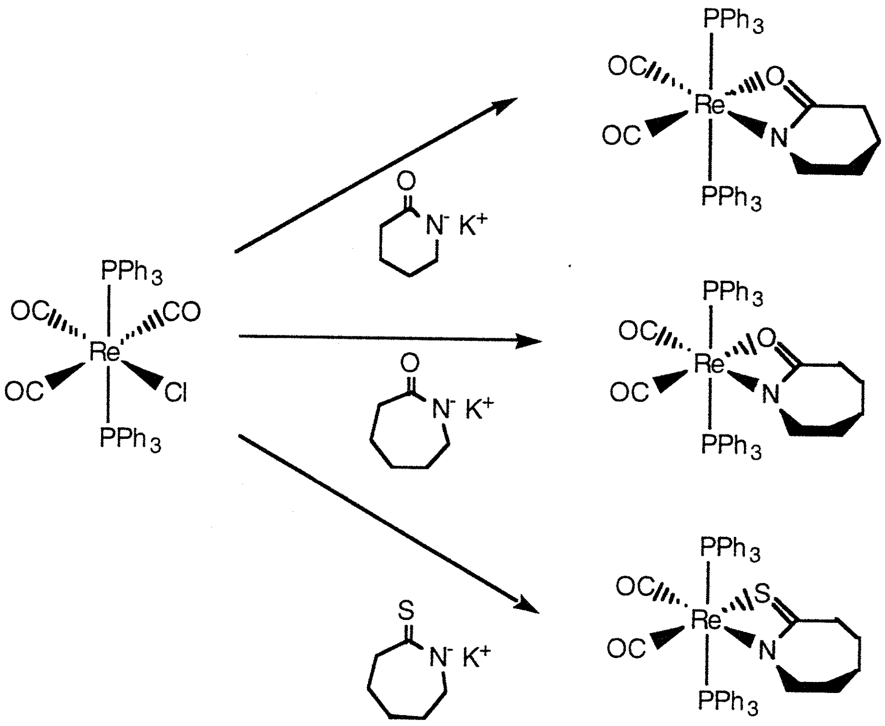

PPh3
OC
CO
Re
OC
Cl
PPh3
N⁻ K⁺
O
S
PPh3
OC
Re
O
N
S
OC
PPh3

Table 1: Crystallographic Data for (**1**).

Complex	$C_{51}H_{48}NO_3P_2Re$
Molecular weight	971.10
Wavelength	0.71073 Å, Mo Kα
Temperature, °C	-86
Crystal color, habit	yellow, prismatic
Crystal dimensions	0.280 x 0.280 x 0.360 mm
Crystal system	Triclinic
Space group	$P\bar{1}$
a, Å	12.102(2)
b, Å	13.981(2)
c, Å	14.011(2)
α, °	97.57(3)
β, °	112.51(3)
γ, °	94.71(3)
V, Å^3	2148(2)
Z	2
Density (calculated), g/cm^3	1.501
Absorption coefficient, cm^{-1}	29.8
F(000)	980
Diffractometer	Enraf-Nonius CAD-4
Scan Type	ω-2θ
2θ max	49.9°
Reflections Collected	7936
Unique data	7542
Absorption Correction	Lorentz-polarization

Max. and Min. Transmissions	0.79 and 1.49
Refinement Method	Full-matrix least-squares
Data/ parameters	6096 / 523
Goodness of Fit on F^2	2.43
R	0.067
R_w	0.073
Largest diff. peak and hole	2.25 and -2.54 eÅ^{-3}

Table 2: Atomic Coordinates for **(1)**.

	x	y	z	B(eq)
Re	0.21358(5)	0.25856(4)	0.23588(5)	1.72(2)
P(1)	0.0543(3)	0.1588(3)	0.2542(3)	1.9(1)
P(2)	0.3723(3)	0.3633(2)	0.2201(3)	2.0(1)
O(1)	0.2586(9)	0.0842(7)	0.1108(8)	4.1(4)
O(2)	0.387(1)	0.2055(9)	0.4379(8)	5.5(5)
O(3)	0.077(1)	0.3125(8)	0.0980(9)	4.7(5)
N(1)	0.124(1)	0.3898(9)	0.254(1)	2.8(4)
C(1)	0.528(1)	0.347(1)	0.300(1)	1.9(4)
C(2)	0.556(1)	0.254(1)	0.315(1)	2.3(5)
C(3)	0.671(1)	0.242(1)	0.374(1)	2.8(5)
C(4)	0.764(1)	0.320(1)	0.419(1)	3.2(6)
C(5)	0.738(1)	0.412(1)	0.406(1)	3.0(5)
C(6)	0.619(1)	0.428(1)	0.346(1)	2.8(5)
C(7)	0.376(1)	0.351(1)	0.088(1)	2.3(5)
C(8)	0.485(1)	0.377(1)	0.077(1)	3.3(6)
C(9)	0.483(1)	0.370(1)	-0.024(1)	3.4(6)
C(10)	0.379(1)	0.334(1)	-0.111(1)	3.7(6)
C(11)	0.273(1)	0.310(1)	-0.099(1)	4.3(6)
C(12)	0.271(1)	0.319(1)	-0.000(1)	2.7(5)
C(13)	0.370(1)	0.4948(9)	0.255(1)	1.9(4)
C(14)	0.396(1)	0.532(1)	0.360(1)	2.8(5)
C(15)	0.400(1)	0.630(1)	0.391(1)	3.5(6)
C(16)	0.376(1)	0.689(1)	0.318(1)	3.8(6)
C(17)	0.356(2)	0.656(1)	0.222(1)	4.5(7)

C(18)	0.347(1)	0.558(1)	0.187(1)	2.7(5)
C(19)	-0.097(1)	0.1683(9)	0.164(1)	1.9(4)
C(20)	-0.187(1)	0.1947(9)	0.194(1)	2.4(5)
C(21)	-0.301(1)	0.204(1)	0.116(1)	2.5(5)
C(22)	-0.324(1)	0.183(1)	0.011(1)	2.9(5)
C(23)	-0.236(1)	0.155(1)	-0.020(1)	2.6(5)
C(24)	-0.124(1)	0.148(1)	0.053(1)	2.4(5)
C(25)	0.069(1)	0.0298(8)	0.2404(9)	1.5(4)
C(26)	-0.005(1)	-0.042(1)	0.158(1)	3.2(6)
C(27)	0.018(1)	-0.137(1)	0.155(1)	3.3(6)
C(28)	0.110(1)	-0.166(1)	0.228(1)	2.8(5)
C(29)	0.186(1)	-0.097(1)	0.313(1)	3.7(6)
C(30)	0.164(1)	-0.000(1)	0.317(1)	2.9(5)
C(31)	0.046(1)	0.1793(9)	0.3849(9)	1.7(4)
C(32)	-0.029(1)	0.1135(9)	0.408(1)	2.1(4)
C(33)	-0.037(1)	0.125(1)	0.504(1)	2.7(5)
C(34)	0.032(1)	0.209(1)	0.578(1)	3.6(6)
C(35)	0.104(1)	0.273(1)	0.557(1)	3.2(5)
C(36)	0.112(1)	0.259(1)	0.459(1)	2.4(5)
C(37)	0.243(1)	0.151(1)	0.163(1)	2.2(4)
C(38)	0.320(1)	0.226(1)	0.360(1)	3.1(5)
C(39)	0.073(2)	0.377(1)	0.162(1)	4.4(7)
C(40)	-0.036(2)	0.442(1)	0.096(1)	5.7(8)
C(41)	-0.131(1)	0.457(1)	0.131(1)	6.0(8)
C(42)	-0.089(2)	0.510(1)	0.243(1)	5.1(7)
C(43)	-0.006(2)	0.465(1)	0.334(1)	5.7(8)
C(44)	0.118(1)	0.467(2)	0.326(1)	7.0(9)

C(45)	0.378(1)	0.058(1)	0.801(1)	2.9(5)
C(46)	0.475(1)	0.012(1)	0.793(1)	3.0(5)
C(47)	0.501(1)	0.015(1)	0.705(1)	3.7(6)
C(48)	0.423(2)	0.052(1)	0.620(1)	4.6(7)
C(49)	0.329(2)	0.O9l(1)	0.629(1)	4.8(7)
C(50)	0.305(1)	0.093(1)	0.716(1)	3.7(6)
C(51)	0.353(1)	0.057(1)	0.895(1)	3.7(6)

Table 3: Bond Lengths in Å of (**1**).

Re	P(1)	2.399(3)	C(9)	C(10)	1.37(2)
Re	P(2)	2.415(3)	C(10)	C(11)	1.37(2)
Re	O(3)	2.28(1)	C(11)	C(12)	1.38(2)
Re	N(1)	2.24(1)	C(13)	C(14)	1.41(2)
Re	C(37)	1.84(1)	C(13)	C(18)	1.35(2)
Re	C(38)	1.87(2)	C(14)	C(15)	1.38(2)
P(1)	C(19)	1.81(1)	C(15)	C(16)	1.36(2)
P(1)	C(25)	1.82(1)	C(16)	C(17)	1.27(2)
P(1)	C(31)	1.86(1)	C(17)	C(18)	1 .37(2)
P(2)	C(1)	1.84(1)	C(19)	C(20)	1.36(2)
P(2)	C(7)	1.86(1)	C(19)	C(24)	1.44(2)
P(2)	C(13)	1.84(1)	C(20)	C(21)	1.43(2)
O(1)	C(37)	1.18(1)	C(21)	C(22)	1.37(2)
O(2)	C(38)	1.17(2)	C(22)	C(23)	1.37(2)
O(3)	C(39)	1.20(2)	C(23)	C(24)	1.38(2)
N(1)	C(39)	1.18(2)	C(25)	C(26)	1.37(2)
N(1)	C(44)	1.40(2)	C(25)	C(30)	1.38(2)
C(1)	C(2)	1.38(2)	C(26)	C(27)	1.38(2)
C(1)	C(6)	1.41(2)	C(27)	C(28)	1.33(2)
C(2)	C(3)	1.36(2)	C(28)	C(29)	1.38(2)
C(3)	C(4)	1.38(2)	C(29)	C(30)	1.40(2)
C(4)	C(5)	1.36(2)	C(31)	C(32)	1.39(2)
C(5)	C(6)	1.42(2)	C(31)	C(36)	1.37(2)
C(7)	C(8)	1.41(2)	C(32)	C(33)	1.37(2)
C(7)	C(12)	1.38(2)	C(33)	C(34)	1.41(2)

C(8)	C(9)	1.39(2)	C(34)	C(35)	1.35(2)
C(35)	C(36)	1.39(2)			
C(39)	C(40)	1.69(2)			
C(40)	C(41)	1.43(2)			
C(41)	C(42)	1.51(2)			
C(42)	C(43)	1.53(2)			
C(43)	C(44)	1.55(2)			
C(45)	C(46)	1.41(2)			
C(45)	C(50)	1.37(2)			
C(45)	C(51)	1.46(2)			
C(46)	C(47)	1.39(2)			
C(47)	C(48)	1.40(2)			
C(48)	C(49)	1.34(2)			
C(49)	C(50)	1.36(2)			

Table 4: Bond Angles in degrees of (**1**).

P(1)	Re	P(2)	178.2(1)
P(1)	Re	O(3)	90.7(3)
P(1)	Re	N(1)	89.5(3)
P(1)	Re	C(37)	89.5(4)
P(1)	Re	C(38)	87.9(4)
P(2)	Re	O(3)	88.9(3)
P(2)	Re	N(1)	88.9(3)
P(2)	Re	C(37)	92.3(4)
P(2)	Re	C(38)	92.2(4)
O(3)	Re	N(1)	56.7(4)
O(3)	Re	C(37)	98.8(5)
O(3)	Re	C(38)	172.8(5)
N(1)	Re	C(37)	155.5(5)
N(1)	Re	C(38)	116.2(5)
C(37)	Re	C(38)	88.3(6)
Re	P(1)	C(19)	115.1(4)
Re	P(1)	C(25)	113.3(4)
Re	P(1)	C(31)	116.4(4)
C(19)	P(1)	C(25)	106.6(6)
C(19)	P(1)	C(31)	103.7(6)
C(25)	P(1)	C(31)	100.2(5)
Re	P(2)	C(1)	115.9(4)
Re	P(2)	C(7)	116.2(4)
Re	P(2)	C(13)	114.6(4)
C(1)	P(2)	C(7)	100.8(6)

C(1)	P(2)	C(13)	103.9(6)
C(15)	C(16)	C(17)	121(1)
C(16)	C(17)	C(18)	122(1)
C(13)	C(18)	C(17)	120(1)
P(1)	C(19)	C(20)	124(1)
P(1)	C(19)	C(24)	117.6(9)
C(20)	C(19)	C(24)	118(1)
C(19)	C(20)	C(21)	120(1)
C(20)	C(21)	C(22)	121(1)
C(21)	C(22)	C(23)	120(1)
C(22)	C(23)	C(24)	120(1)
C(19)	C(24)	C(23)	121(1)
P(1)	C(25)	C(26)	126(1)
P(1)	C(25)	C(30)	118.3(9)
C(26)	C(25)	C(30)	116(1)
C(25)	C(26)	C(27)	121(1)
C(26)	C(27)	C(28)	123(1)
C(27)	C(28)	C(29)	118(1)
C(28)	C(29)	C(30)	119(1)
C(25)	C(30)	C(29)	123(1)
P(1)	C(31)	C(32)	120.1(9)
P(1)	C(31)	C(36)	121.0(9)
C(32)	C(31)	C(36)	119(1)
C(31)	C(32)	C(33)	122(1)
C(32)	C(33)	C(34)	117(1)
C(33)	C(34)	C(35)	122(1)
C(34)	C(35)	C(36)	120(1)

C(7)	P(2)	C(13)	103.3(6)
Re	O(3)	C(39)	86(1)
Re	N(1)	C(39)	88(1)
Re	N(1)	C(44)	145(1)
C(39)	N(1)	C(44)	126(2)
P(2)	C(1)	C(2)	120(1)
P(2)	C(1)	C(6)	120(1)
C(2)	C(1)	C(6)	120(1)
C(1)	C(2)	C(3)	120(1)
C(2)	C(3)	C(4)	122(1)
C(3)	C(4)	C(5)	119(1)
C(4)	C(5)	C(6)	121(1)
C(1)	C(6)	C(5)	118(1)
P(2)	C(7)	C(8)	120(1)
P(2)	C(7)	C(12)	119.8(9)
C(8)	C(7)	C(12)	120(1)
C(7)	C(8)	C(9)	119(1)
C(8)	C(9)	C(10)	121(1)
C(9)	C(10)	C(11)	120(1)
C(10)	C(11)	C(12)	121(1)
C(7)	C(12)	C(11)	120(1)
P(2)	C(13)	C(14)	117(1)
P(2)	C(13)	C(18)	125(1)
C(14)	C(13)	C(18)	118(1)
C(13)	C(14)	C(15)	119(1)
C(14)	C(15)	C(16)	119(1)
C(31)	C(36)	C(35)	120(1)

Re	C(37)	O(1)	176(1)
Re	C(38)	O(2)	179(1)
O(3)	C(39)	N(1)	128(2)
O(3)	C(39)	C(40)	107(2)
N(1)	C(39)	C(40)	124(1)
C(39)	C(40)	C(41)	119(1)
C(40)	C(41)	C(42)	115(2)
C(41)	C(42)	C(43)	120(1)
C(42)	C(43)	C(44)	107(2)
N(1)	C(44)	C(43)	114(1)
C(46)	C(45)	C(50)	118(1)
C(46)	C(45)	C(51)	120(1)
C(50)	C(45)	C(51)	122(1)
C(45)	C(46)	C(47)	119(1)
C(46)	C(47)	C(48)	120(1)
C(47)	C(48)	C(49)	118(2)
C(48)	C(49)	C(50)	123(2)
C(45)	C(50)	C(49)	121(1)

Figure 3: PLUTO representation of Re(CO)$_2$(PPh$_3$)$_2$(C$_5$H$_{10}$NCO) showing atom labelling schemes.

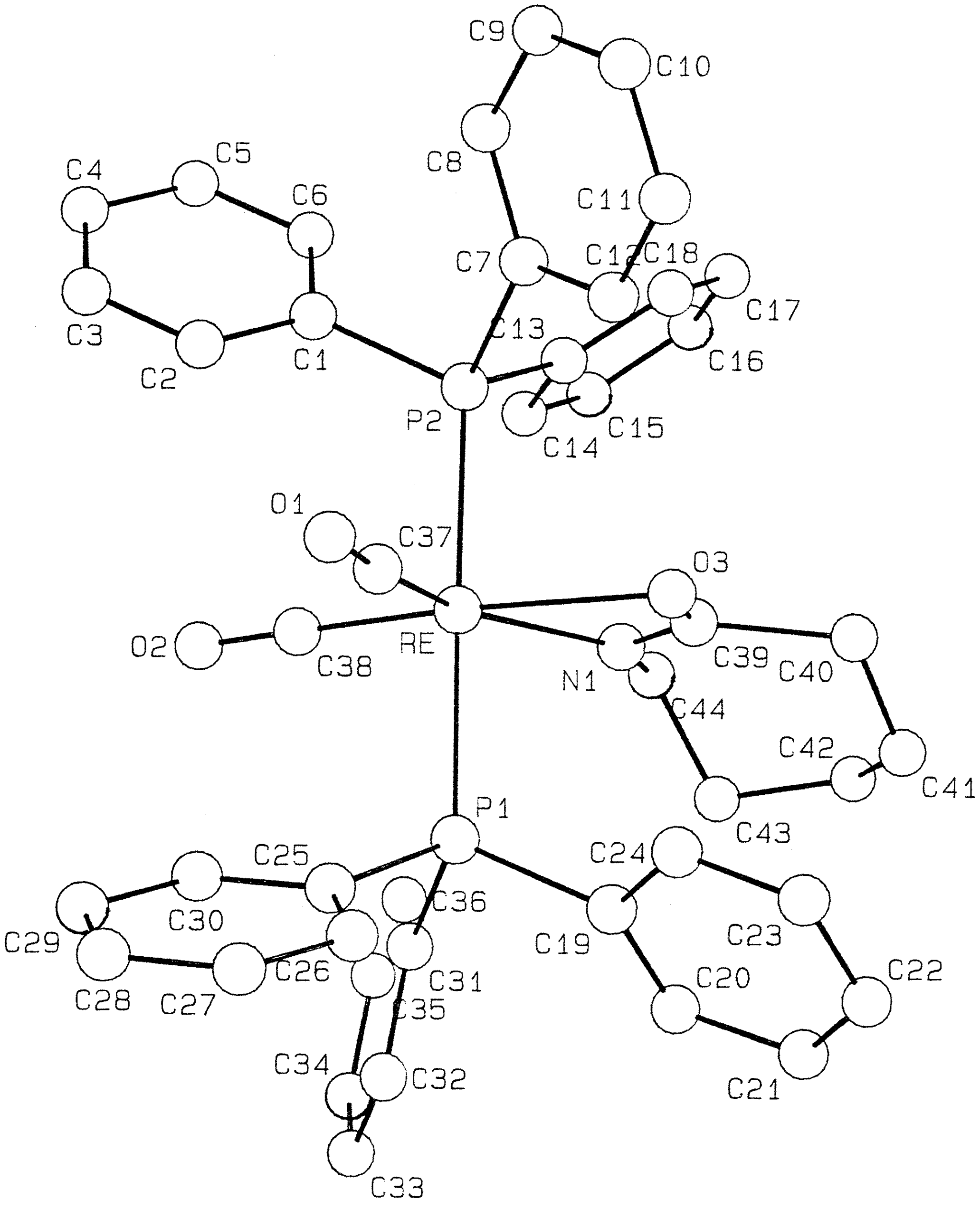
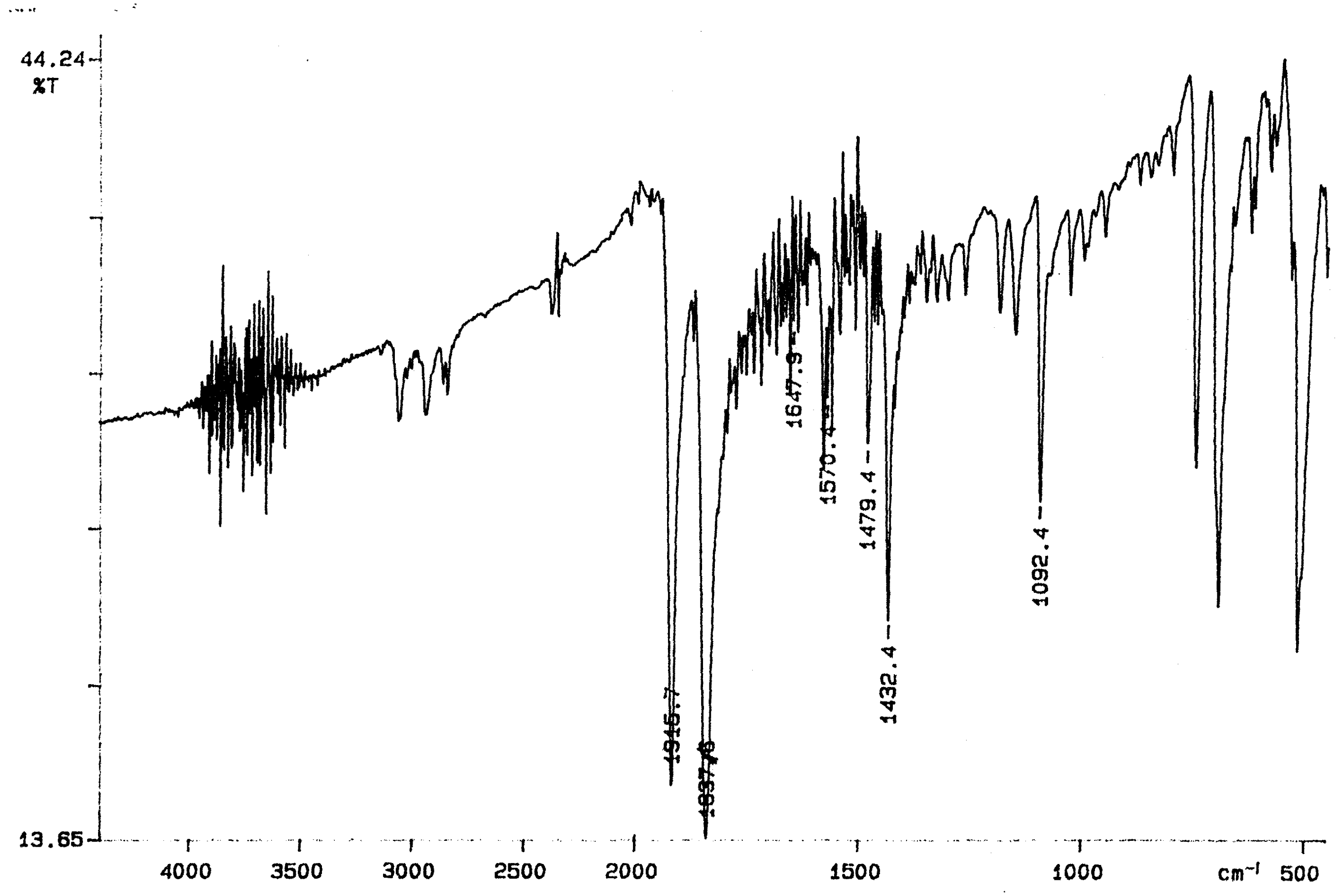

C9
C10
C8
C4
C5
C6
C11
C7
C12
C18
C17
C3
C13
C16
C2
C1
P2
C15
C14
O1
C37
O3
O2
C38
RE
C39
C40
N1
C44
C42
C41
C43
P1
C25
C24
C36
C30
C19
C23
C29
C26
C31
C22
C28
C27
C20
C35
C34
C32
C21
C33

Figure 4: FTIR Spectrum of $Re(CO)_2(PPh_3)_2(C_4H_8NCO)$ in KBr.



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msh122b/kcl

CHAPTER 5

Reactions of Technetium and Rhenium with 2-Hydrazinoimidizoline

Introduction

The examples in the literature and in the previous chapters have been complexes synthesized from potentially chelating hydrazines in which an extended π-system is present in the chelating organohydrazide. It has been proposed that this π-system is responsible for the diamagnetic behavior of the complexes. The potentially chelating organohydrazine 2-hydrazinoimidizoline does not contain an aromatic ring unlike the pyridine and pyrimidine hydrazines. The absence of the aromatic ring may perturb the π-system formed upon chelation with the metal, and as a result, the products may not have the same diamagnetic behavior that is seen with the aromatic, chelating organohydrazide complexes.

Experimental

Preparation of $Tc(NNC_3H_5N_2)(PPh_3)_2Cl_2$ (1). In a 100 mL rounded bottom flask with a stir bar, 0.5 mL NH_4TcO_4 (aq) (0.4304 M) was evaporated to dryness and redissolved in 10 mL methanol. To the solution, 0.11601 g (0.64083 mmol) 2-hydrazinoimidizoline·HBr was added along with 10 mL methanol and one milliliter of a 0.48 M HCl methanolic solution. The solution darkened immediately to a red-brown color, and 0.17186 g (0.65523 mmol) PPh_3 was added. The reaction mixture was stirred at room temperature for 2.5 hours, at which time a green-golden colored solid was present. The reaction mixture was filtered and washed with methanol. No ^1H NMR spectrum was observed. The solid is soluble in DMF and slightly soluble in CH_2Cl_2. The product decomposes upon recrystallization in $CH_2Cl_2/MeOH/Et_2O$ to $Tc(N)(PPh_3)_2Cl_2$, as observed by X-ray structural analysis. Over a period of days, the product can be observed decomposing to $Tc(N)(PPh_3)_2Cl_2$ in the solid state.

FABMS(+) {in *p*-nitrobenzylalcohol} 791 m/z.
IR (KBr) (cm^{-1}) ν 3162 (N-H), 1595 (s), 1556 (s), 1504 (vs), 1479 (vs), 1433 (vs), 1336 (vs), 1291 (s), 1189, 1091.5 (vs), 1069, 920, 749.5 (s), 694 (s), 520 (s)

Preparation of $Re(NNC_3H_5N_2)(PPh_3)_2Cl_2 \cdot 2HCl$ (2). To a 100 mL rounded bottom flask were added 0.1152 g (0.4217 mmol) $NaReO_4$ and 10 mL methanol. To this solution, 0.2322 g (1.283 mmol) 2-hydrazinoimidizoline·HBr was added along with five milliliters of methanol and one milliliter of a 0.48 M HCl methanolic solution. The reaction mixture was heated for 2 hours, at which time it was a red solution. Triphenylphosphine (0.3452 g, 1.316 mmol) was added, and heating was continued overnight. A green precipitate formed, which was filtered after the reaction mixture cooled to room temperature. The solid was collected and washed with methanol and dried *in vacuo*. The solid is very slightly soluble in dichloromethane.

Anal Calc. for $C_{39}H_{37}Cl_4N_4P_2Re$: C, 49.22; H, 3.92; N, 5.89. Found: C, 49.1; H, 3.8; N, 5.5. FABMS(+) {in *p*-nitrobenzylalcohol} 879 m/z ($Re(NNC_3H_5N_2)(PPh_3)_2Cl_2$).

Preparation of $Tc(NO)(NNC_3H_5N_2)(PPh_3)_2Cl$ (3). To a 100 mL rounded bottom flask with a stir bar were added 0.11746 g (0.15345 mmol) $Tc(NO)(NCMe)(PPh_3)_2Cl_2$ and 10 mL methanol. To the reaction mixture, 0.06331 g (0.3497 mmol) 2-hydrazinoimidizoline·HBr was added along with 10 mL methanol and one milliliter of a 0.48 M HCl methanolic solution. The mixture was stirred at room temperature for one hour at which time 10 mL dichloromethane was added and the reaction heated. The reaction was heated for six hours at which time there was an orange solution and a light colored precipitate. The solid was collected by filtration. The filtrate was kept in a rounded bottom flask for approximately one week. The filtrate darkened in color to a red-brown. The filtrate was reduced in volume to approximately one milliliter, and approximately 50 mL Et_2O were added. A red-brown solid precipitated, and it was filtered and dried *in vacuo*.

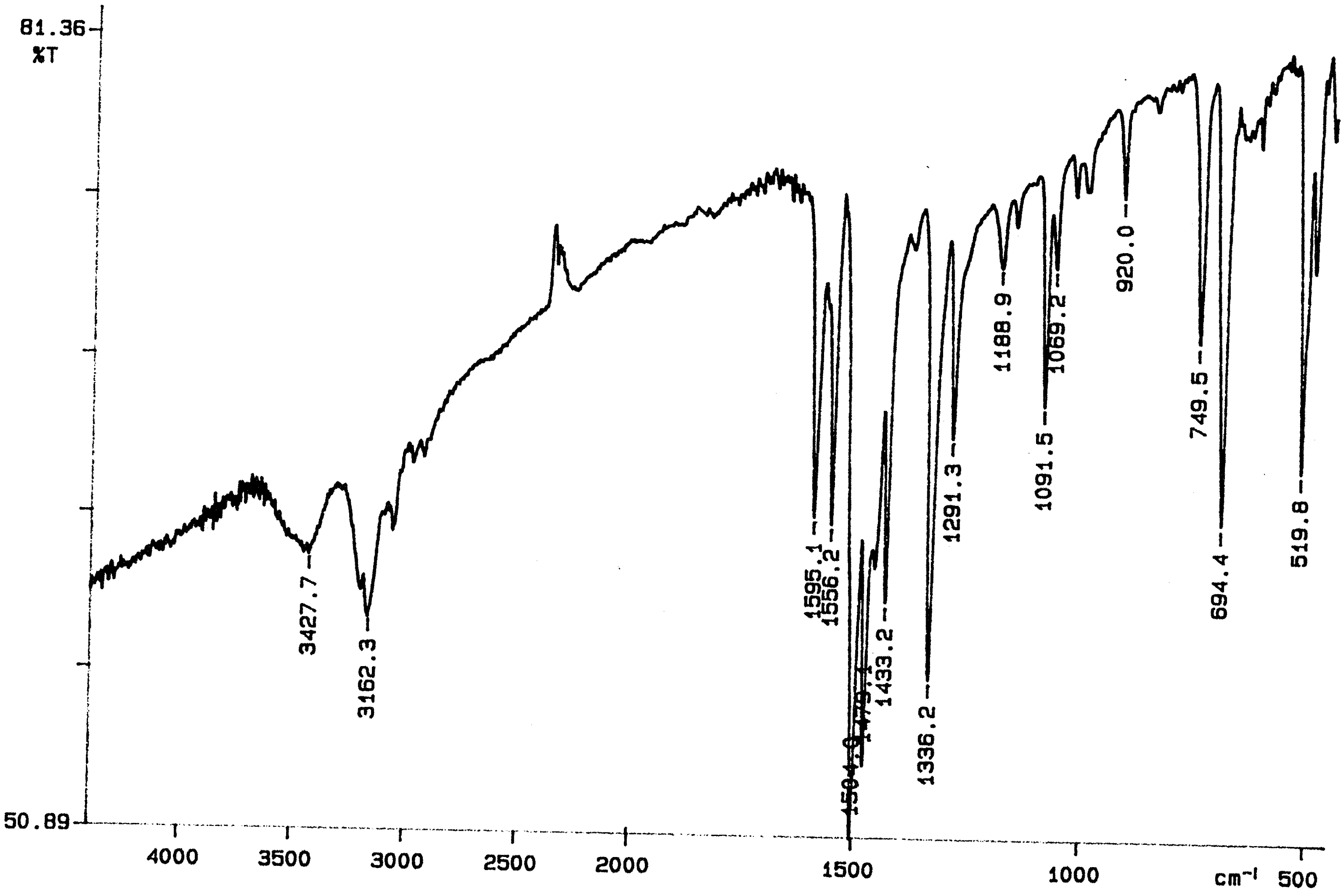
IR (KBr) (cm^{-1}) ν 1743 (N≡O).

FABMS(+) {in *p*-nitrobenzylalcohol} 786 m/z (M+H), 524 ($M-PPh_3$).

Results and Discussion

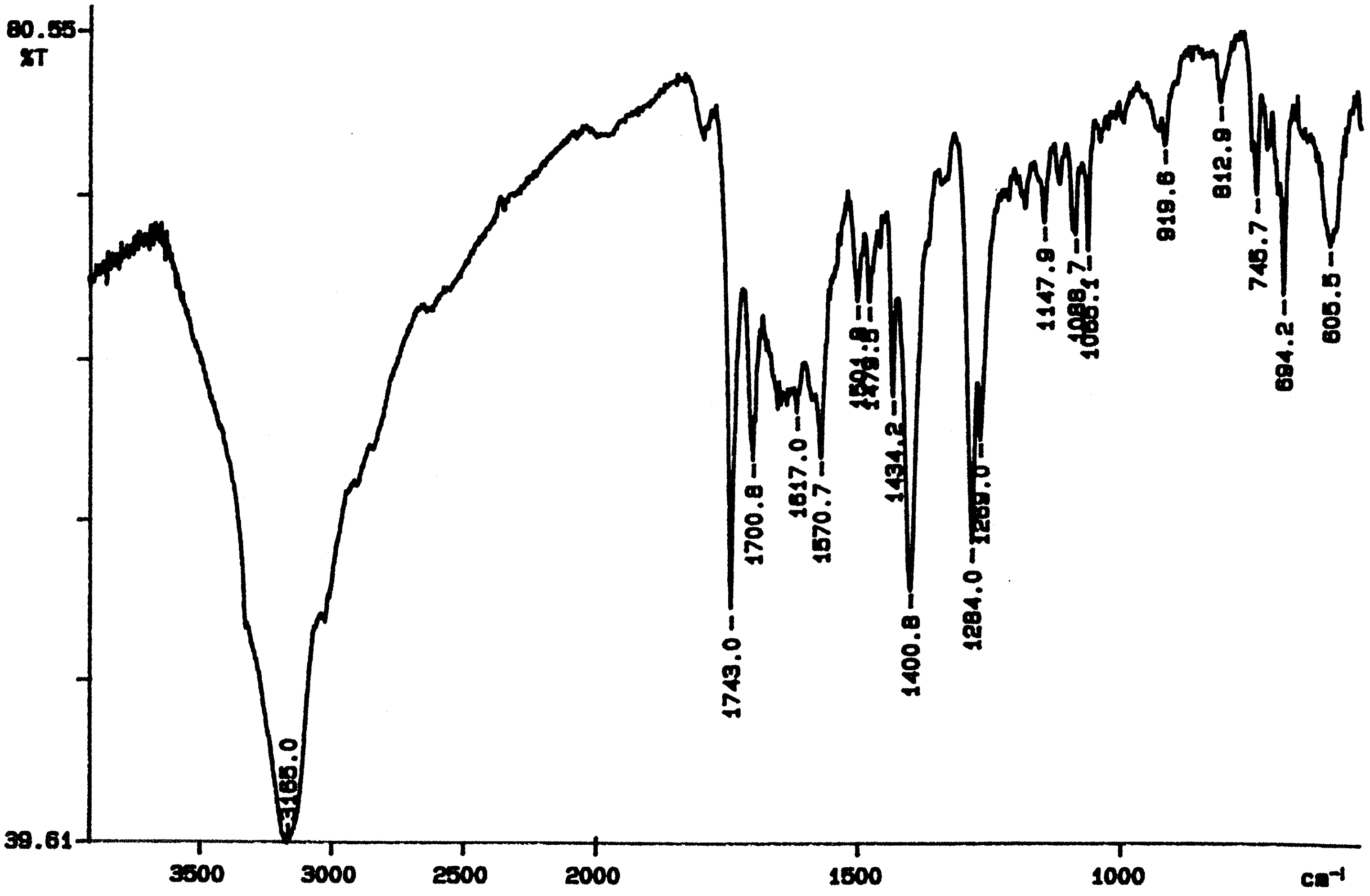
The potentially chelating organohydrazine 2-hydrazinoimidizoline differs from 2-hydrazinopyridine and 2-hydrazinopyrimidine in that the nitrogen containing ring is not aromatic. The lack of aromaticity may diminish the π-system formed with the metal upon chelation. It should be noted that without X-ray structural data, it is not known if the organohydrazide complexes **(1)**, **(2)**, and **(3)** contain a chelated organohydrazide. This hydrazine reacts readily with perrhenate or pertechnetate, and a product can be isolated upon addition of triphenylphosphine. The product is not soluble in most organic solvents but does dissolve readily in DMF. The complex formed upon reaction with $Tc(NO)(NCMe)(PPh_3)_2Cl_2$, **(3)**, is soluble in dichloromethane and methanol.

Figure 1: FTIR of $Tc(NNC_3H_5N_2)(PPh_3)_2Cl_2$ in KBr.



97/01/27 18:52
X: 16 scans, 4.0cm-1
mhk6-11/kbr

Figure 2: FTIR of $Tc(NO)(NNC_3H_5N_2)(PPh_3)_2Cl$ in KBr.



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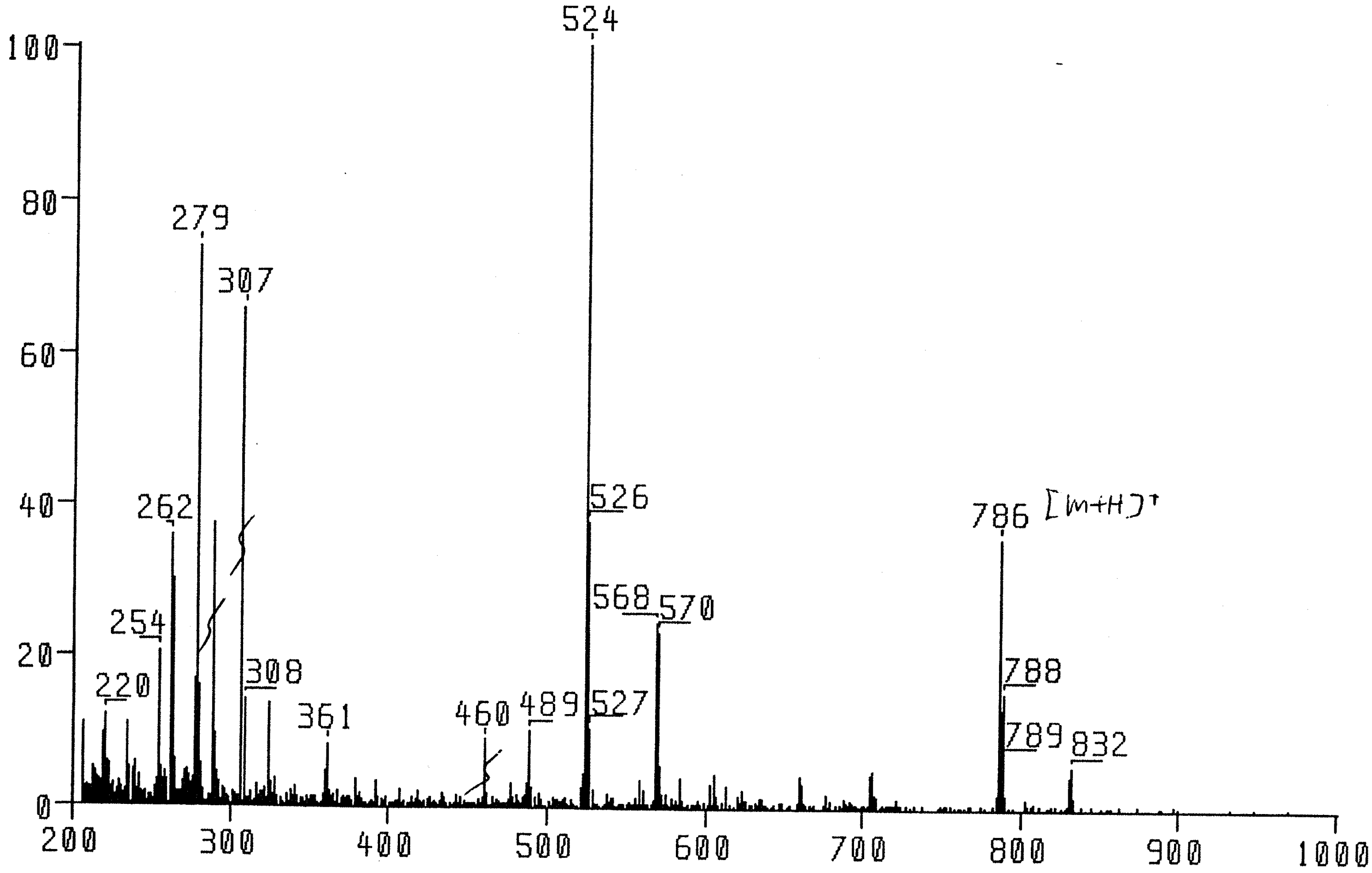
MHK 6-37/KBr

Figure 3: FAB(+) Mass Spectrum of Tc(NO)($NNC_3H_5N_2$)(PPh_3)$_2$Cl.


524
279
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262
254
220
308
361
460
489
527
526
568
570
786
[M+H]+
788
789
832
100
80
60
40
20
0
200
300
400
500
600
700
800
900
1000

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Biographical Note

The author was born on March 11, 1971 in New York, New York. She was raised in Boca Raton, FL. After graduating from Saint Andrew's School, she attended the University of Florida, where she did her undergraduate research with Russell Drago. After receiving her B.S. in chemistry, she came to MIT and worked with Alan Davison.