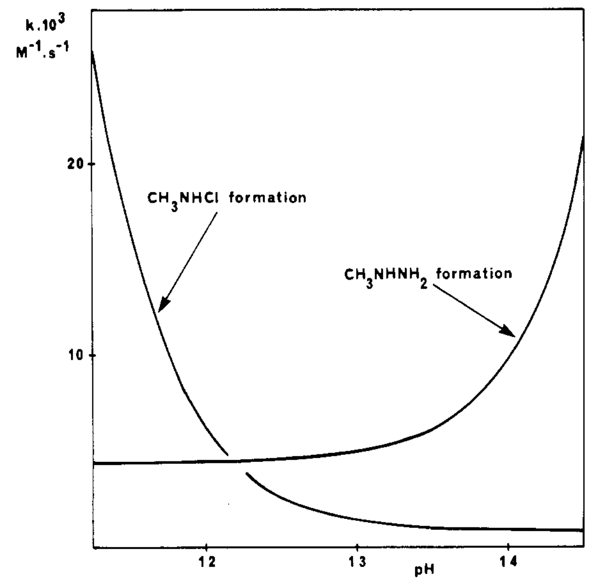


Figure 5. Comparison of the rate constants of formation of CH_3NHCl and CH_3NHNH_2 at 25 °C.

Influence of CH_3NHCl Formation on the Synthesis of CH_3NHNH_2. The comparison of the rate constants for the formation of CH_3NHCl and CH_3NHNH_2 by the reaction of CH_3NH_2 and NH_2Cl is shown in Figure 5.

From the plotted curves, it can be seen that below pH 11, CH_3NHCl is formed preferably to CH_3NHNH_2, while for pH > 14, CH_3NHCl is a minor product compared to CH_3NHNH_2.

In the pH range 11–14, CH_3NHNH_2 and CH_3NHCl are produced in comparable amounts. Then, if CH_3NHNH_2 is prepared at too low a pH, the amount of CH_3NHCl can be appreciable. For instance, at pH 14, the ratio of methylhydrazine to methylchloramine is equal to 11, while for pH 13 it is equal to 3.5. So, to prepare CH_3NHNH_2, a high pH value is required.

However, in practice, another reaction should be taken into account: oxidation of methylhydrazine by chloramine, which is acid- and base-catalyzed[27,28] and the influence of which leads us to adjust the pH near 13.8–14 to obtain the highest yields in CH_3NHNH_2.[28]

Conclusion

This study confirms the experimental results of Snyder and Margerum about the transfer of chlorine between chloramine and methylamine. It shows that the evolution of the rate constant with pH can be interpreted in terms of buffer-assisted reactions, involving molecule/molecule and ion/molecule interactions.

In order to analyze more closely the mechanism of the reaction, the influence of the nature of the amine has been studied at the present time.

Finally, the chlorine-transfer reaction must be taken into account in the kinetic model governing the synthesis of CH_3NHNH_2 by the Raschig process.

Registry No. NH_2Cl, 10599-90-3; CH_3NH_2, 74-89-5.

---

(27) Ferriol, M.; Gazet, J.; Cohen-Adad, M. T. *Bull. Soc. Chim. Fr.* **1984**, I-180.

(28) Giudice, M.; Ferriol, M.; Saugier-Cohen Adad, M.-T. To be submitted for publication.

Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, and Department of Radiology, Harvard Medical School and Brigham and Women's Hospital, Boston, Massachusetts 02115

Synthesis, Spectroscopy, and Structural Characterization of Five-Coordinate, Bis(aryldiazenido)technetium Complexes and Their Protonation Reactions. X-ray Structure of $[TcCl(PPh_3)_2(NNC_6H_4Br)_2]$

Terrence Nicholson,[1] Nadine de Vries,[1a] Alan Davison,*[,1a] and Alun G. Jones[1b]

Received January 17, 1989

The reaction of $[TcCl_4(PPh_3)_2]$ with arylhydrazines in methanol yields $[TcCl(PPh_3)_2(NNPh)_2]$ (**1**). Complex **1** displays trigonal-bipyramidal geometry with phosphine ligands occupying axial sites. The technetium–aryldiazenido moieties are nearly equivalent, with Tc–N–N bond angles of 166.2 (6) and 170.7 (7)° and multiple bonding throughout. The chloride ligand occupies the remaining equatorial coordination site. The addition of HCl(g) to complex **1** in methanol gives the neutral, six-coordinate "hydrazido(2–)" complex $[TcCl_2(PPh_3)_2(NNPh)(NNHPh)]$. The reaction of complex **1** with HBr(g) gives the doubly protonated, cationic species $[TcBr_2(PPh_3)_2(NNPh)(NHNHPh)](Br)$. The ^{99}Tc NMR spectra for these species are presented, which suggest that the metals exhibit considerable Tc(V) character and that the formal oxidation states of -1 and $+1$ are not accurate descriptions of the electron density on the technetium. The ^1H NMR, mass, and electronic spectroscopic data are also presented for the various species, along with the crystal structure of the five-coordinate bis(aryldiazenido) precursor. Crystal data for $C_{48}H_{38}N_4P_2ClBr_2Tc$: monoclinic space group $P2_1/n$, $a = 12.174$ (2) Å, $b = 19.008$ (3) Å, $c = 20.162$ (3) Å, $\beta = 106.39$ (1)°, $V = 4476$ (1) Å^3 to give $Z = 4$. Structure solution and refinement based on 4135 reflections converged at $R = 0.053$ and $R_w = 0.062$.

Introduction

The search for new technetium complexes for use in diagnostic nuclear medicine continues to be an active area of research. As the basic coordination chemistry of technetium rapidly unfolds, an increasing emphasis is being placed on complexes incorporating easily functionalized ligands.

Technetium nitrosyl chemistry has been studied with a variety of coligands.[2] However complexes that incorporate the organodiazenido ligand, a species isoelectronic with the nitrosyl ligand, have yet to be reported. Both species are geometrically versatile. However the organodiazenido ligand has the added capacity to be easily functionalized.

Aryldiazenido ligands, M—N=NR units with sp^2 hybridization on the β-nitrogen, may display a number of structural conformations (see Figure 1).[3] In the "singly bent" conformation (I), it can be considered either formally a neutral, 3-electron-donor ligand or a 2-electron-donating, monocationic ligand. The latter is the convention we have adopted throughout this work. In the "doubly bent" mode of coordination (II), it serves formally as a 2-electron-donating, monoanionic ligand.

Both the α- and β-nitrogens in the aryldiazenido moiety are basic and susceptible to protic attack. The products of the pro-

---

(1) (a) Massachusetts Institute of Technology. (b) Harvard Medical School and Brigham and Women's Hospital.

(2) Brown, D. S.; Newman, J. L.; Thornback, J. R.; Davison, A. *Acta Crystallogr.* **1987**, *C43*, 1692. Linder, K. E.; Davison, A.; Dewan, J. C.; Costello, C. E.; Maleknia, S. *Inorg. Chem.* **1986**, *25*, 2085. Abram, U.; Kirmse, R.; Kohler, K.; Lorenz, B.; Kaden, L. *Inorg. Chim. Acta* **1987**, *129*, 15.

(3) Nicholson, T.; Zubieta, J. *Polyhedron* **1988**, *7*, 171. Nicholson, T.; Zubieta, J. A. *J. Chem. Soc., Chem. Commun.* **1985**, 367.

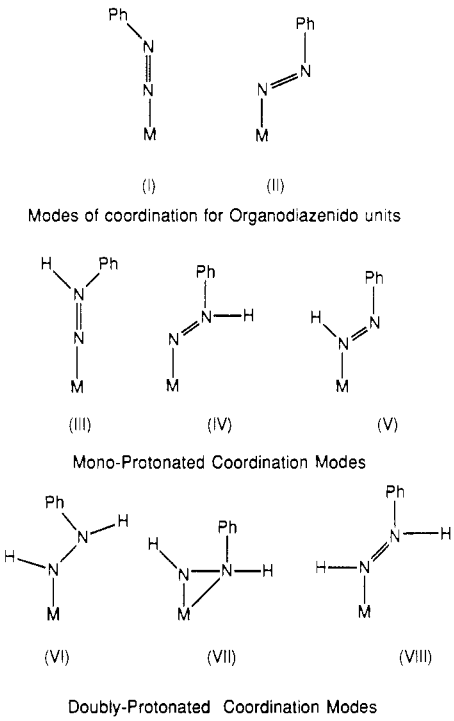


Figure 1. Various coordination modes for the organodiazenido ligand and species generated by its protonation reactions.

tonation reactions frequently show intermediate M–N and N–N bond lengths and bond angles not accurately reflecting a specific hybridization. Consequently, nomenclature for these derivatives can be specious. The protonation of the β-nitrogen on the aryldiazenido unit generates what is referred to as the isodiazene or the "hydrazido(2–)" ligand. The hydrazido(2–) ligand, like the aryldiazenido unit, may display linear (III), or bent (IV) M–N–N frameworks. The bent hydrazido(2–) ligand is, by the convention adopted here, a neutral, 2-electron-donating ligand. The proton may also reside on the metal-bound nitrogen of the aryldiazenido unit, generating the "aryldiazene" ligand (V). The addition of a second proton generates what is termed the "hydrazido(1–)" unit, which in theory contains an N–N single bond. This doubly protonated species may also adopt several conformations including the "end-on" geometry (VI), which is formally a 2-electron-donating, monoanionic ligand. It may also coordinate in a "side-on" manner (VII). Frequently however, structural studies show multiple bond character between the N–N linkage (VIII), which is more accurately described as a protonated form of the isodiazene unit.[3]

Experimental Section

Caution! ^{99}Technetium is a weak β-emitter. All work has been done in laboratories approved for the use of low levels of radioactive materials. Precautions have been detailed elsewhere.[4]

Ammonium pertechnetate was supplied as a gift from Du Pont Biomedical Products. Reagents and solvents were used as received unless otherwise specified. Column chromatography was performed by using Keisel TLC grade silica gel. Infrared spectra were obtained on a Mattson Cygnus 100 FTIR instrument, and electronic spectra were recorded on an HP 8451A diode-array spectrometer. ^{1}H NMR spectra were recorded on a Varian XL-300 FT NMR spectrometer. ^{99}Tc NMR spectra were recorded on a Varian VXR 500 FT NMR instrument and were referenced to $[\mathrm{TcO_4}]^-$. Fast atom bombardment mass spectra of samples dissolved in a p-nitrobenzyl alcohol matrix were recorded with a MAT 731 mass spectrometer equipped with an Ion Tech B11N FAB gun and 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, Atlanta, GA.

Syntheses. The green, methanol-insoluble complex $[\mathrm{TcCl_4(PPh_3)_2}]$ was prepared by the literature method.[5]

$[\mathrm{TcCl(PPh_3)_2(NNC_6H_4\text{-}\mathit{p}\text{-}Br)_2}]$ (1). A mixture of (p-bromophenyl)hydrazine hydrochloride (0.92 g), $[\mathrm{TcCl_4(PPh_3)_2}]$ (0.21 g), and diisopropylethylamine (1.15 g) was warmed gently in 200 mL of methanol for 30 min. The resulting brown solution was concentrated to about 50 mL by using rotary evaporation. The resulting yellow-brown precipitate was isolated, washed with methanol, and dried under vacuum. It was then dissolved in a minimum amount of dichloromethane and chromatographed on a silica column, eluting with methylene chloride. A single yellow component eluted, leaving a brown insoluble fraction near the top of the column. The eluted material was concentrated to a golden-brown oil by using rotary evaporation. The oil was then dissolved in dichloromethane and carefully layered with methanol and diethyl ether, which yielded a bright orange, crystalline complex (**1**) upon standing at room temperature. Yield: 55–65%. Anal. Calcd for $\mathrm{C_{48}H_{38}N_4Br_2ClP_2Tc}$: C, 56.13; H, 3.74; N, 5.46. Found: C, 55.95; H, 3.74; N 5.46. IR (KBr): $\nu(\mathrm{N{=}N}) = 1518, 1573\ \mathrm{cm^{-1}}$. FABMS(+): m/z = 1027 ($\mathrm{M^+}$), 991 ($\mathrm{M^+}$ – Cl), 8.43 ($\mathrm{M^+}$ – $\mathrm{NNC_6H_4Br}$), 623 ($\mathrm{Tc(PPh_3)_2^+}$), 361 ($\mathrm{Tc(PPh_3)^+}$).

$[\mathrm{TcCl(PPh_3)_2(NNC_6H_4\text{-}\mathit{p}\text{-}OMe)_2}]$ (2). The bis((p-methoxyphenyl)diazenido) complex (**2**) was prepared analogously to compound **1** by substituting (p-methoxyphenyl)hydrazine hydrochloride. After the mixture was refluxed in methanol for 30 min, a bright yellow precipitate formed, which was washed with methanol and dried under vacuum. The yellow precipitate was dissolved in methylene chloride and chromatographed on silica. A single yellow-orange band was eluted with methylene chloride, to which 15 mL of methanol was added. The resulting mixture was evaporated on a rotary evaporator, which caused the formation of a bright orange precipitate as the methanol concentration increased. Yield: 50–60%. Anal. Calcd for $\mathrm{C_{50}H_{44}N_4O_2P_2ClTc}$: C, 64.62; H, 4.77; N, 6.03. Found: C, 64.72; H, 4.79; N, 5.74. IR (KBr): $\nu(\mathrm{N{=}N}) = 1520, 1577\ \mathrm{cm^{-1}}$. UV-vis (benzene): $\lambda_{\max} = 282$ ($\epsilon = 4.9 \times 10^4$), 394 nm ($\epsilon = 9.6 \times 10^3$). ^{1}H NMR ($\mathrm{CD_2Cl_2}$, 22 °C): δ 3.72–3.78 (3 s, 6 H, $\mathrm{ArOC}\mathit{H}_3$), 7.15–7.40 (m, 38 H, Ar H). ^{1}H NMR ($\mathrm{CD_2Cl_2}$, –50 °C): δ 3.67–3.75 (4 s, 6 H, $\mathrm{ArOC}\mathit{H}_3$), 6.5–7.6 (m, 38 H, Ar H). ^{99}Tc NMR ($\mathrm{CDCl_3}$, 22 °C): δ 470. FABMS(+): m/z 929 ($\mathrm{MH^+}$), 893 ($\mathrm{M^+}$ – Cl), 793 ($\mathrm{M^+}$ – $\mathrm{NNC_6H_4OMe}$), 623 ($\mathrm{Tc(PPh_3)_2^+}$), 361 ($\mathrm{Tc(PPh_3)^+}$).

$[\mathrm{TcCl_2(PPh_3)_2(NNC_6H_4\text{-}\mathit{p}\text{-}Br)(NNHC_6H_4\text{-}\mathit{p}\text{-}Br)}]$ (3). The bright orange complex **1** was suspended in methanol. Gaseous HCl was bubbled into the stirred suspension by using a gas dispersion tube until all material dissolved, giving a deep red solution. The solvent was then removed by rotary evaporation, and the resulting red oil was dissolved in a minimum amount of dichloromethane. The red solution was then layered with methanol that had been briefly exposed to HCl(g) and then carefully layered with diethyl ether. Dark red crystals appeared gradually when the mixture was allowed to stand at room temperature. Yield: 70–75%. Anal. Calcd for $\mathrm{C_{48}H_{39}N_4Br_2Cl_2P_2Tc}$: C, 54.19; H, 3.71; N, 5.26. Found: C, 53.98; H, 3.76; N, 5.23. IR (KBr): $\nu(\mathrm{N{=}N}) = 1570, 1665\ \mathrm{cm^{-1}}$.

$[\mathrm{TcCl_2(PPh_3)_2(NNC_6H_4\text{-}\mathit{p}\text{-}OMe)(NNHC_6H_4\text{-}\mathit{p}\text{-}OMe)}]$ (4). Dark red complex **4** was prepared analogously to complex **3**. The orange bis(aryldiazenido) complex (**2**) was suspended in methanol and exposed to gaseous HCl until the formation of a deep purple solution. The resulting solution was then concentrated to a red oil with rotary evaporation and dissolved in a minimum amount of methylene chloride. Deep red crystals of **4** as a bis(methanol) solvate formed gradually when the solution was layered with slightly acidified methanol followed by diethyl ether. Yield: 75–80%. Anal. Calcd for $\mathrm{C_{52}H_{53}N_4O_4P_2Cl_2Tc}$: C, 60.51; H, 5.19; N, 5.45. Found: C, 60.62; H, 5.01; N, 5.37. IR (KBr): $\nu(\mathrm{N{=}N}) = 1565, 1658\ \mathrm{cm^{-1}}$. UV-vis ($\mathrm{CHCl_3}$): $\lambda_{\max} = 500$ nm ($\epsilon = 1.5 \times 10^4$). ^{1}H NMR ($\mathrm{CDCl_3}$, 22 °C): δ 3.76–3.82 (2 s, 6 H, $\mathrm{ArOC}\mathit{H}_3$), 6.2–7.9 (m, 38 H, Ar H), 13.8 (s, 1 H, $\mathrm{TcNN}\mathit{H}\mathrm{Ar}$). ^{1}H NMR ($\mathrm{CDCl_3}$, –50 °C): δ 3.73–3.82 (2 s, 6 H, $\mathrm{ArOC}\mathit{H}_3$), 6.1–8.0 (m, 38 H, Ar H), 13.7 (s, 1 H, $\mathrm{TcNN}\mathit{H}\mathrm{Ar}$). ^{99}Tc NMR ($\mathrm{CDCl_3}$, 22 °C): δ 940.

$[\mathrm{TcCl_2(PPh_3)_2(NNC_6H_4OMe)(NHNHC_6H_4OMe)}]\mathrm{(Cl)}$ (5). The purple doubly protonated, ionic species was synthesized from complex **2** dissolved in chloroform. Brief exposure of the yellow solution to gaseous HCl caused a rapid color change to deep purple. The purple compound was never isolated as a solid for analytical, mass, or infrared spectral analysis. UV-vis ($\mathrm{CHCl_3}$): $\lambda_{\max} = 552$ nm ($\epsilon = 2.7 \times 10^4$). ^{1}H NMR ($\mathrm{CDCl_3}$, 22 °C): δ 3.93–4.96 (2 s, 6 H, $\mathrm{ArOC}\mathit{H}_3$), 6.50–7.95 (m, 38 H, Ar H), 12.85 (s, 1 H, $\mathrm{TcNHN}\mathit{H}\mathrm{Ar}$). ^{1}H NMR ($\mathrm{CDCl_3}$, –50 °C): δ 3.79–3.84 (2 s, 6 H, $\mathrm{ArOC}\mathit{H}_3$), 6.2–7.9 (m, 38 H, Ar H), 12.7 (d, 1 H, $\mathrm{TcNHN}\mathit{H}\mathrm{Ar}$), 14.95 (d, 1 H, $\mathrm{Tc}\mathit{H}\mathrm{NNHAr}$). ^{99}Tc NMR ($\mathrm{CDCl_3}$, 22 °C): δ 910.

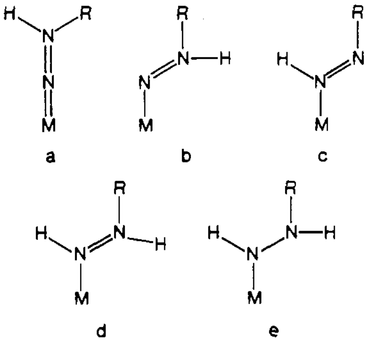
$[\mathrm{TcBr_2(PPh_3)_2(NNC_6H_5)(NNC_6H_5)(NHNHC_6H_5)}]\mathrm{(Br)}$ (6). The precursor used to synthesize complex **6** was prepared similar to complex **1**, with the same stoichiometric excess of phenylhydrazine and diiso-

---

[4] Davison, A.; Orvig, C.; Trop, H. S.; Sohn, M.; DePamphilis, B. V.; Jones, A. G. *Inorg. Chem.* **1980**, *19*, 1988.

[5] Mazzi, U.; De Paoli, G.; Di Bernardo, P.; Magon, L. *J. Inorg. Nucl. Chem.* **1976**, 721.

Table I. Structural and ^1H NMR Data for Organohydrazide N-H Protons



structure	complex	bond lengths, Å M-N	N-N	M-N-N bond angle, deg	δ(N-H), ppm	solvent
a	$[ReCl_2(PPh_3)_2(NH_3)(NN\mathit{H}Ph)](Br)$[16]	1.75	1.28	172	4.92	CD_2Cl_2
	$[ReCl_2(PPh_3)_2(NHNHCOPh)(NN\mathit{H}COPh)]$[3]	1.73	1.27	174	1.30	CD_2Cl_2
b	$[ReBr_2(PPh_3)_2(NNPh)(NN\mathit{H}Ph)]$[8]	1.92	1.29	131	12.3	
	$[Mo\{SC(Ph)N(Me)O\}_2(NNCOPh)(NHN\mathit{H}COPh)]$[14]	1.94	1.36	132	12.5	$CDCl_3$
	$[TcCl_2(PPh_3)_2(NNAr)(NN\mathit{H}Ar)]$				13.7	$CDCl_3$
c	$[PtCl(PEt_3)_2(N\mathit{H}NPh)](ClO_4)$[13]	1.97	1.24	125	15.1	
	$[Re(CO)_2(cp)(N\mathit{H}NMePh)](BF_4)$[15]	1.95	1.32	139	16	$CDCl_3$
	$[Mo\{SC(Ph)N(Me)O\}_2(NNCOPh)(N\mathit{H}NHCOPh)]$[14]	1.94	1.36	132	15.9	$CDCl_3$
d	$[Ir(CO)(PPh_3)_2(N\mathit{H}N\mathit{H}Ar)](BF_4)$[19]	1.91	1.39	119	12.7; 14.2	acetone-d_6
	$[TcCl_2(PPh_3)_2(NNAr)(N\mathit{H}N\mathit{H}Ar)](Cl)$				12.7; 14.9	$CDCl_3$
e	$[ReCl_2(PPh_3)_2(N\mathit{H}N\mathit{H}COPh)(NNHCOPh)]$[3]	2.21	1.44	119	6.2; 9.8	CD_2Cl_2

propylethylamine as used for the synthesis of complex **1**. The product isolated from this reaction, a dark yellow powder, was suspended in dichloromethane and precipitated with the addition of methanol as a golden yellow powder. The yellow material was then suspended in dry methanol and HBr(g) added, similar to the procedure used for the synthesis of complex **4**. The red solution gave dark red crystals of complex **6** when layered with diethyl ether. Yield: 55–65%. Anal. Calcd for $C_{48}H_{42}N_4Br_3P_2Tc$: C, 53.6; H, 3.94; N, 5.21. Found: C, 54.2; H, 4.07; N, 5.23. IR (KBr): $\nu(N{=}N) = 1669, 1793\ cm^{-1}$.

NMR Sample Preparation. The proton NMR studies were performed exclusively on the (*p*-methoxyaryl)diazenido complexes whose singly and doubly protonated derivatives can be distinguished visually. The sample used for the ^1H NMR spectra of complex **2** was prepared by dissolving an analytically pure sample of complex **2** in CD_2Cl_2. Samples of the protonated species were prepared in $CDCl_3$ by passing HCl(g) over the dissolved sample until color change occurred. The singly protonated species, complex **4**, is present when the red color is retained. The doubly protonated species, complex **5**, is present when the deep purple color develops. Samples were filtered through cotton plugs into the NMR tubes to minimize the aqueous and HCl contaminants introduced during the protonation reactions. The ^1H NMR spectra, recorded at both ambient temperature and −50 °C, confirmed the presence of the desired species.

X-ray Crystallographic Data Collection Parameters. The crystal data and experimental details of the structure determination are given in Table II. The crystal exhibited no significant decay under X-ray irradiation.

Dull orange prismatic crystals of complex **1** were isolated from methylene chloride–methanol–diethyl ether as described above. The crystal selected for the X-ray study measured 0.15 × 0.20 × 0.35 mm. The diffractometer employed was a Rigaku AFC-6R instrument. The scan mode used was $\omega-2\theta$, with a maximum 2θ of 55.1°. The quadrant collected was $+h,+k,+l$. The reflections collected were $h0l$ ($h + l \neq 2n$) and $0k0$ ($k \neq 2n$) giving a total of 11 133 reflections. Of those, 10 643 were unique, and 4136 reflections with $I > 3\sigma(I)$ were used in the final structure refinement. An empirical absorption correction using the DIFABS/TEXSAN software of the Molecular Structure Corp. was employed. The technetium atom was located by using direct methods. Hydrogen atom positions were calculated. Neutral atomic scattering factors were used throughout the analysis.[6] Extinction effects were not observed.

Results and Discussion

In recent years there has been a renewed interest in transition-metal complexes that incorporate the organodiazenido ligand. Rhenium in particular shows a rich and varied coordination chemistry with organohydrazines.[3,7] Parallel chemistry with technetium, rhenium's second-row congener, has been slower to develop. Because of the increased emphasis on the basic coordination chemistry of technetium, a result of its expanding role in diagnostic nuclear medicine, we sought to extend the organohydrazine chemistry to technetium.

Table II. X-ray Data for Structure Determination of **1**

empirical formula	$C_{48}H_{38}N_4P_2ClBr_2Tc$
fw	1025.06
cryst syst	monoclinic
a, Å	12.174 (2)
b, Å	19.008 (3)
c, Å	20.162 (3)
β, deg	106.39 (1)
V, Å^3	4476 (1)
space group	$P2_1/n$ (No. 14)
Z	4
D(calcd), g/cm^3	1.521
D(exptl), g/cm^3	1.45
μ, cm^{-1}	23.72
radiation[a] (λ, Å)	Mo Kα (0.710 69)
temp, °C	23
T_{max}, T_{min}	1.09, 0.91
R, R_w	0.052, 0.062
goodness of fit	1.48

[a] Graphite monochromated.

Syntheses. There are a variety of methods available for the introduction of the aryldiazenido ligand. The silylated aryldiazene $Me_3SiNNPh$ has been shown to be an efficient reagent.[8] Aryldiazonium salts can also be efficient reagents for the synthesis of aryldiazenido complexes. Another method involves the reaction of arylhydrazines and a noncoordinating base with an appropriate transition-metal precursor.

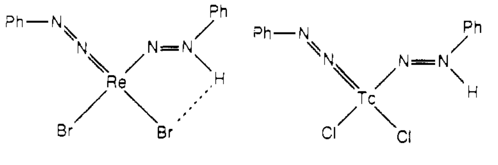
If the latter method is employed, the technetium(IV) complex $[TcCl_4(PPh_3)_2]$ reacts with an excess of (*p*-bromophenyl)hydrazine hydrochloride and diisopropylethylamine in methanol to give $[TcCl(NNC_6H_4\text{-}p\text{-}Br)_2(PPh_3)_2]$ (**1**) as a dull orange crystalline product after chromatographic purification. The complex exhibits

---

(6) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol IV.

(7) Nicholson, T.; Zubieta, J. *Inorg. Chem.* **1987**, *26*, 2094. Hsieh, T. C.; Nicholson, T.; Zubieta, J. *Inorg. Chem.* **1988**, *27*, 241.

(8) Dilworth, J. R.; Harrison, S. A.; Walton, D. R. M.; Schweda, E. *Inorg. Chem.* **1985**, *24*, 2594.



$[ReBr_2(PPh_3)_2(NNPh)(NNHPh)]$ $[TcCl_2(PPh_3)_2(NNPh)(NNHPh)]$

Figure 2. Schematic showing the hydrogen bonding present in $[ReBr_2(PPh_3)_2(NNAr)(NNHAr)]$[7] that is not present in $[TcCl_2(PPh_3)_2(NNAr)(NNHAr)]$.

strong IR bands[9a] at 1518 and 1573 cm^{-1} tentatively assigned to ν(N=N) from the diazenido units, virtually identical with those for the rhenium analogue.[9]

The analogous rhenium complex $[ReCl(PPh_3)_2(NNC_6H_4Br)_2]$ was synthesized from the rhenium(V) precursor $[ReOCl_3(PPh_3)_2]$, under similar reaction conditions,[10] while the manganese analogue $[MnCl(PPh_3)_2(NNPh)_2]$ has been synthesized from the reaction of $[Mn(CO)_2(NNPh)(PPh_3)_2]$ with benzenediazonium hexafluorophosphate.[11]

The yellow complex **1** reacts with excess HCl(g) in methanol at room temperature to give a dark red crystalline material, which elemental analysis shows to be $[TcCl_2(PPh_3)_2(NNC_6H_4Br)(NNHC_6H_4Br)]$ (**3**). The singly protonated complex **3** exhibits strong IR bands at 1665 and 1570 cm^{-1} assigned to ν(N=N) from the bent hydrazido(2–) and diazenido ligands. The values reported for the analogous rhenium complex are 1620 and 1570 cm^{-1}.[8] The structurally characterized rhenium complex was shown to be protonated at the β-nitrogen of the diazenido unit and to adopt a bent conformation with a hydrogen bond between the N–H proton and one of the metal-bound bromine atoms. The difference in the higher frequency N=N absorption in the IR spectra may reflect the fact that in the technetium complex, the protonated aryldiazenido ligand is unable to hydrogen bond to the chloride ligand as shown in Figure 2. The hydrogen bond in the rhenium complex stabilizes a bent conformation with a M–N–N bond angle of 131.2 (10)°, which is reflected in the ν(N=N) of the IR. The infrared spectra of the singly protonated rhenium[7] and technetium complexes are similar in not showing an absorption in the ν(N–H) region.[9b]

Trialkylammonium chloride is sufficiently acidic to convert the yellow five-coordinate species to the red singly protonated species in methanol at room temperature. However, trialkylammonium hexafluorophosphate fails to react at room temperature in methanol, with the yellow precursor remaining insoluble. These results suggest that the incorporation of the second chloride ligand is necessary for the formation of the β-protonated, bent hydrazido(2–) species, complex **4**. This chemistry closely parallels the cobalt–nitrosyl chemistry of Enemark and Feltham[12] in which a change in coordination number from five to six, through the incorporation of a thiocyanate ligand, results in a cationic, linear nitrosyl ligand adopting a bent geometry where it serves as an anionic ligand.

The reaction of the bis(phenyldiazenido) complex $[TcCl(PPh_3)_2(NNC_6H_5)_2]$ with HBr(g) in benzene allows isolation of the doubly protonated, cationic "hydrazido(1–)" species $[TcBr_2(PPh_3)_2(NNC_6H_5)(NHNHC_6H_5)](Br)$, complex **6**, in which bromines have replaced the coordinated chloride ligand. The five-coordinate rhenium complex $[ReCl(PPh_3)_2(NNPh)_2]$ also undergoes the halide-exchange reaction in the presence of HBr.[8] However the product isolated from the reaction of the rhenium precursor and HBr in methanol was the singly protonated, neutral complex $[ReBr_2(PPh_3)_2(NNC_6H_5)(NNHC_6H_5)]$. The insolubility of complex **6** in benzene and toluene lends support to its assignment as an ionic species. The infrared spectrum of the doubly protonated complex **6** shows ν(N=N) at 1793 and 1669 cm^{-1}.[9c] Methanol is sufficiently basic to deprotonate both the singly and doubly protonated species, converting them to the yellow, five-coordinate, bis(aryldiazenido) complexes.

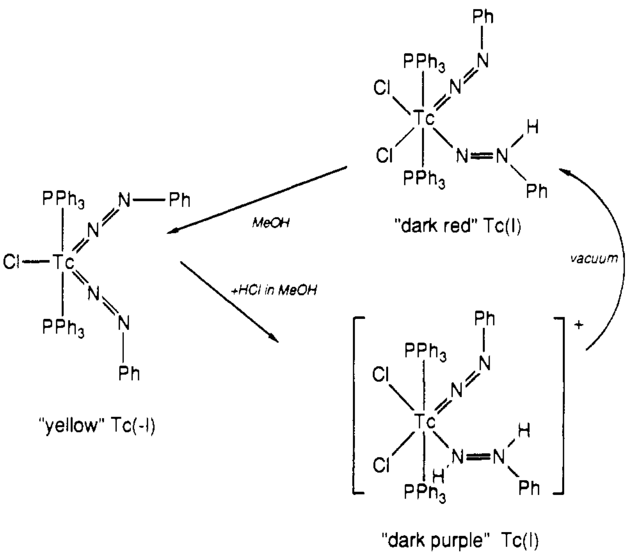


Figure 3. Schematic showing the protonation reactions and products for $[TcCl(PPh_3)_2(NNAr)_2]$.

Electronic Spectroscopy. The protonation chemistry was complicated by the fact that, with the phenyldiazenido complex $[TcCl(PPh_3)_2(NNPh_2)]$ and the (*p*-bromophenyl)diazenido derivative, both the singly and doubly protonated species are dark red and difficult to distinguish. To inductively perturb the M=N=N—Ar linkage, the (*p*-methoxyphenyl)diazendo complex **2** was prepared. The bis((*p*-methoxyaryl)diazenido) complex is a golden yellow color. However, its singly protonated derivative, complex **4**, and doubly protonated derivative, complex **5**, are easily distinguishable.

A suspension of complex **2** in methanol exposed to gaseous HCl gave the methanol-soluble, doubly protonated hydrazido(1–) complex **5**, which is a deep purple color. When this purple solution was evaporated under vacuum, 1 equiv of HCl was removed, to give the dark red, six-coordinate, neutral monoprotonated complex **4**. When the red complex **4** was dissolved in dichloromethane and layered with methanol, the second equivalent of HCl was lost, regenerating the yellow, five-coordinate complex **2**. (See the reaction scheme, Figure 3).

The electronic spectrum of complex **2** in benzene has a single, weak band in the visible region at 394 nm. After a brief exposure to gaseous HCl, a second band appears at 500 nm associated with complex **4**. A solution of complex **2** in a more polar solvent such as chloroform, when exposed to HCl(g), shows the formation of the 500-nm band. Treatment with additional HCl causes the 500-nm band to disappear, while a new band associated with the chloroform-soluble, doubly protonated, ionic species, complex **5**, emerges at 552 nm. The electronic spectroscopy of the five-coordinate complex and the products from its protonation reactions are listed in the Experimental Section.

Mass Spectrometry. The fast-atom-bombardment mass spectrum (FABMS) of complex **1** shows the protonated parent ion, (MH^+), at *m/z* 1027. Loss of hydrogen chloride generates a peak at *m/z* 991. The loss of one of the aryldiazenido units generates a peak at *m/z* 843. There are also peaks present assigned to $[Tc(PPh_3)_2]^+$, *m/z* 623, and $[Tc(PPh_3)]^+$, *m/z* 361. The spectra

---

(9) Unpublished results. (a) IR absorptions for $[TcCl(PPh_3)_2(NNC_6H_4Br)_2]$: 500 (m), 506 (m), 516 (s), 692 (s), 707 (w), 745 (m), 833 (w), 1007 (w), 1069 (m), 1094 (m), 1401 (w), 1432 (s), 1473 (vs), 1518 (vs), 1549 (s), 1573 (w), 1592 (m) cm^{-1}. (b) IR absorptions for $[TcCl_2(PPh_3)_2(NNC_6H_4Br)(NNHC_6H_4Br)]$: 497 (m), 514 (vs), 693 (vs), 741 (m), 824 (m), 1002 (m), 1067 (s), 1092 (s), 1158 (w), 1187 (w), 1374 (s), 1434 (vs), 1478 (vs), 1570 (s), 1665 (vs) cm^{-1}. (c) IR absorptions for $[TcBr_2(PPh_3)_2(NNC_6H_5)(NHNHC_6H_5)](Br)$: 511 (vs), 693 (vs), 744 (s), 1093 (m), 1337 (w), 1434 (vs), 1481 (s), 1575 (s), 1669 (m), 1793 (m) cm^{-1}.

(10) Nicholson, T.; Lombardi, P.; Zubieta, J. *Polyhedron* **1987**, *6*, 1577.

(11) Haymore, B. *J. Organomet. Chem.* **1977**, *137*, C11.

(12) Enemark, J. H.; Feltham, R. D. *Proc. Natl. Acad. Sci. U.S.A.* **1972**, *69*, 3534. Enemark, J. H.; Feltham, R. D. *J. Am. Chem. Soc.* **1974**, *96*, 5002. Enemark, J. H.; Feltham, R. D. *J. Am. Chem. Soc.* **1974**, *96*, 5004. Enemark, J. H.; Feltham, R. D.; Riker-Nappier, J.; Bizot, K. F. *Inorg. Chem.* **1975**, *14*, 625.

of the protonated complexes only show peaks that correspond to the five-coordinate, bis(aryldiazenido) species. This reflects the ease with which the N–H protons are removed and the reversibility of the protonation reactions. The solvent used to run the mass spectra was *p*-nitrobenzyl alcohol, which like methanol is sufficiently basic to cause deprotonation. An analogous fragmentation pattern is seen for the (*p*-methoxyaryl)diazenido derivative. The mass spectrometric results for complex **2** are listed in the Experimental Section.

^{1}H NMR Spectra. The N–H proton from the singly protonated complex **4**, $[TcCl_2(PPh_3)_2(NNC_6H_4OMe)(NNHC_6H_4OMe)]$, gives rise to a singlet at 13.7 ppm in the room-temperature spectrum, while at −50 °C, the signal appears at 13.8 ppm. The analogous rhenium complex $[ReBr_2(PPh_3)_2(NNPh)(NNHPh)]$,[8] whose N–H proton was shown crystallographically to reside on the β-nitrogen of the "bent" hydrazido(2−) ligand, gives rise to a signal at 12.3 ppm at room temperature. The alternate site for the initial protonation is an α-nitrogen, giving an aryldiazene complex. The N–H proton residing on the metal-bound nitrogen of the structurally characterized platinum aryldiazene complex $[PtCl(PEt_3)_2(NHNC_6H_4F)](ClO_4)$ gives rise to a signal at 15.1 ppm in the ^{1}H NMR spectrum.[13] Other structurally characterized complexes containing protonated ligands with N–H protons residing on the α-nitrogen give rise to signals at 15.9[14] and 16 ppm.[15] While the N–H signal from complex **4** appears midway between the signals of the rhenium hydrazido(2−) complex and platinum aryldiazene complex, we assume, based on the NMR data of the doubly protonated species (vide supra), that the singly protonated technetium complex is structurally similar to the rhenium complex. The third possible conformation of the singly protonated reaction product is a linear hydrazido(2−) species. However, ^{1}H NMR signals from the N–H protons of these species appear at much lower frequencies, 4.92[16] and 1.3 ppm.[3]

The NMR and IR data for complex **5** suggest that the doubly protonated ligand is similar in geometry to VIII in Figure 1, with significant nitrogen–nitrogen multiple-bond character. The ^{1}H NMR spectrum of complex **5** at −50 °C in dry CD_2Cl_2 shows a pair of well-defined doublets at 12.7 and 14.95 ppm from the doubly protonated "hydrazido(1−)" ligand. The signal at 14.95 ppm is likely from the α-N–H proton, similar to the N–H proton in the aryldiazene platinum complex. The integration of the two doublets from complex **5** shows the expected 1:1 ratio.

The literature contains two examples of structurally characterized doubly protonated diazenido complexes with ^{1}H NMR data similar to those of complex **5**. The ^{1}H NMR spectrum of the bent "hydrazido(1−)" complex $[Mo(N_2COPh)(NHNHCOPh)(PhCSNMeO)_2]$[14] shows a pair of doublets at 15.85 and 10.2 ppm from the N–H protons. The nitrogen–nitrogen bond for the doubly protonated ligand of the molybdenum complex is 1.361 (7) Å, which along with a Mo–N–N bond angle of 131.9 (3)° confirms the presence of only partial N–N double bond character. The ^{1}H NMR data for complex **5** is also similar to those for the iridium complex $[Ir(CO)(PPh_3)_2(NHNHPh)](BF_4)$.[17] The doubly protonated ligand in this complex is orthometalated, which undoubtedly influences its geometry. The N–H protons give signals at 12.7 and 14.2 ppm. The X-ray structure establishes Ir–N and N–N bond lengths of 1.912 (10) and 1.388 (13) Å, respectively, and an Ir–N–N bond angle of 119.1 (8)°. Table I shows chemical shifts for the N–H protons of various complexes containing ligands of this type with bond lengths and angles associated with the appropriate ligand.

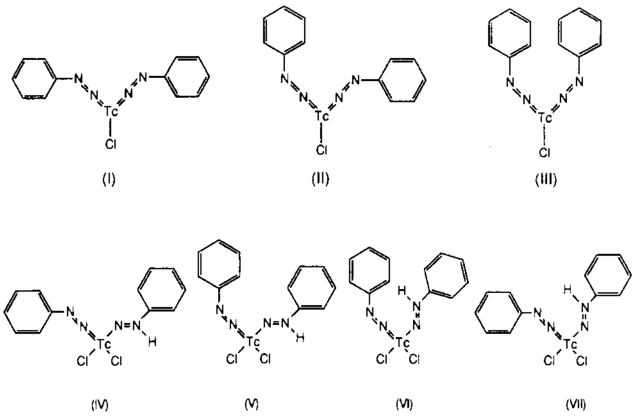


Figure 4. Schematic depicting the conformational isomerism apparent in the ^{1}H NMR of bis((*p*-methoxyphenyl)diazenido) complexes.

The chemical shifts reported for the only example of N–H protons in a doubly protonated complex with an N–N single bond are 6.2 and 9.8 ppm,[3] while those from complexes with side-bound ligands are at 4 and 7 ppm.[18] This effectively rules out these coordination modes for the doubly protonated ligand in complex **5**.

The H–H coupling observed for the N–H protons in complex **5** is 14.5 Hz, significantly higher than the 10.2 Hz reported for the N–H protons of the molybdenum complex.[14] The values reported for other structurally characterized complexes of this nature fall in the 10.5–12.5-Hz range,[19] with corresponding N–N bond lengths of 1.35–1.39 Å. Complexes with coordinated neutral hydrazines, $M–NH_2–NHR$ with a N–N single bond, show 8-Hz H–H coupling constants for the N–H protons,[20] which is lower than the values reported for complexes of intermediate nitrogen–nitrogen double-bond character. The established trend in H–H coupling constants suggests that complex **5** contains an N–N bond order of nearly 2.

It is interesting to note that the ^{1}H NMR spectra of complexes **4** and **5** are water-sensitive. The only N–H signal apparent in the room-temperature spectrum of doubly protonated complex **5** in $CDCl_3$ that was not rigorously dried is a singlet at 12.8 ppm. These protons were shown by magnetization transfer experiments to be exchanging with the water in solution (1.8 ppm). This phenomenon has been reported previously for complexes containing ligands of this type[15] and suggests that, in wet solvents, the N–H protons are rapidly exchanging with protons in solution. The fact that only one of the N–H protons gives rise to a signal at room-temperature indicates further that the second N–H proton is exchanging more rapidly than the first.

The ^{1}H NMR spectrum of the five-coordinate complex **2** at room temperature shows three signals arising from the methoxy C–H protons on the aryldiazenido ligands near 3.6 ppm. This reflects the presence of only two of the three possible conformations expected for of the bis(aryldiazenido) complexes (see Figure 4). Conformation III is apparently too sterically encumbered in the equatorial plane, a result of the close proximity of the coplanar diazenido–aryl groups. The X-ray crystal data presented for complex **2**, vide infra, confirms the presence of conformation II.

The room temperature and −50 °C ^{1}H NMR spectra of complexes **4** and **5** show a pair of signals near 3.9 ppm that arise from the inequivalent C–H methoxy protons on the aryl groups of the protonated and non-protonated aryldiazo ligands. This suggests that only one of the possible conformational isomers of the singly and doubly protonated species are present in solution, which is

---

(13) Ittel, S. D.; Ibers, J. A. *J. Am. Chem. Soc.* **1974**, *96*, 4804. Parshall, G. W. *J. Am. Chem. Soc.* **1967**, *89*, 1822. Krogsrud, S.; Ibers, J. A. *Inorg. Chem.* **1975**, *9*, 2298. Ittel, S. D.; Ibers, J. A. *Inorg. Chem.* **1975**, *3*, 636.

(14) Fitzroy, M. D.; Frederiksen, J. M.; Murray, K. S.; Snow, M. R. *Inorg. Chem.* **1985**, *24*, 3265.

(15) Barrientos-Penna, C. F.; Campana, C. F.; Einstein, F. W. B.; Jones, T.; Sutton, D.; Tracy, A. S. *Inorg. Chem.* **1984**, *23*, 363.

(16) Douglas, P. G.; Galbraith, A. R.; Shaw, B. L. *Transition Met. Chem.* (*Weinheim, Ger.*) **1975/1976**, *1*, 17. Mason, R.; Thomas, K. M.; Zubieta, J. A.; Douglas, P. G.; Galbraith, A. R.; Shaw, B. L. *J. Am. Chem. Soc.* **1974**, *96*, 260.

(17) Carroll, J. A.; Cobbledick, R. E.; Einstein, F. W. B.; Farrell, D. S.; Vogel, P. L. *Inorg. Chem.* **1977**, *16*, 2462.

(18) Schrock, R. R.; Liu, A. H.; O'Regan, M. B.; Finch, W. C.; Payack, J. F. *Inorg. Chem.* **1988**, *27*, 3574.

(19) McCleverty, J. A.; Rae, A. E.; Wolochowicz, I.; Bailey, N. A.; Smith, J. M. A. *J. Chem. Soc., Dalton Trans.* **1983**, 71.

(20) Rigby, W.; McCleverty, J. A.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1979**, 382.

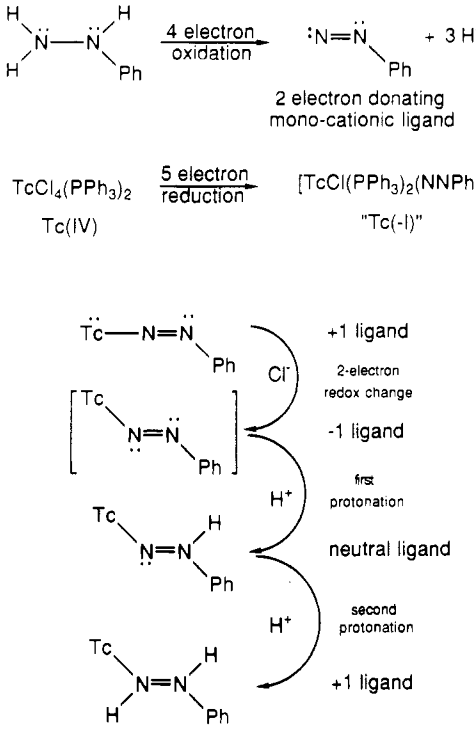


Figure 5. Schematic depicting the redox behavior of the synthetic precursors of complexes **1** and **2**, along with the proposed modes of coordination and oxidation states for the protonated aryldiazenido complexes.

Table III. Atomic Positional Parameters for **1**

atom	*x*	*y*	*z*
Tc1	0.42233 (6)	0.24901 (4)	0.25637 (3)
Br1	0.1357 (1)	0.55509 (7)	−0.00105 (6)
Br2	0.7687 (1)	0.46898 (6)	0.60438 (5)
Cl1	0.4805 (2)	0.1357 (1)	0.3098 (1)
P1	0.5947 (2)	0.2457 (1)	0.2175 (1)
P2	0.2586 (2)	0.2517 (1)	0.3040 (1)
N1	0.3319 (6)	0.2504 (4)	0.1689 (3)
N2	0.2722 (6)	0.2617 (4)	0.1097 (4)
N3	0.4669 (5)	0.3308 (4)	0.2986 (3)
N4	0.4811 (6)	0.3929 (4)	0.3153 (3)
C11	0.5941 (7)	0.3072 (5)	0.1484 (4)
C12	0.543 (1)	0.3724 (6)	0.1472 (5)
C13	0.540 (1)	0.4188 (6)	0.0944 (7)
C14	0.586 (1)	0.4024 (6)	0.0426 (6)
C15	0.634 (1)	0.3390 (6)	0.0431 (5)
C16	0.6386 (8)	0.2910 (5)	0.0945 (5)
C21	0.7234 (7)	0.2662 (5)	0.2875 (5)
C22	0.788 (1)	0.3267 (6)	0.2867 (5)
C23	0.881 (1)	0.3419 (7)	0.3425 (7)
C24	0.907 (1)	0.3002 (9)	0.3988 (6)
C25	0.845 (1)	0.2399 (7)	0.4000 (5)
C26	0.7535 (8)	0.2234 (6)	0.3449 (5)
C31	0.6276 (8)	0.1629 (5)	0.1831 (5)
C32	0.542 (1)	0.1281 (6)	0.1378 (7)
C33	0.561 (1)	0.0651 (7)	0.1058 (8)
C34	0.670 (1)	0.0399 (6)	0.1219 (7)
C35	0.758 (1)	0.0756 (7)	0.1666 (6)
C36	0.735 (1)	0.1365 (6)	0.1973 (5)
C41	0.1728 (7)	0.1730 (4)	0.2974 (4)
C42	0.1858 (7)	0.1178 (5)	0.2559 (5)
C43	0.1212 (8)	0.0585 (5)	0.2511 (5)
C44	0.0405 (8)	0.0534 (5)	0.2858 (5)
C45	0.0272 (8)	0.1066 (6)	0.3290 (5)
C46	0.0926 (8)	0.1653 (5)	0.3331 (5)
C51	0.2969 (7)	0.2735 (4)	0.3959 (4)
C52	0.2321 (7)	0.3173 (4)	0.4256 (4)
C53	0.2677 (9)	0.3299 (5)	0.4958 (5)
C54	0.3638 (8)	0.2995 (6)	0.5365 (4)
C55	0.4277 (9)	0.2573 (6)	0.5088 (4)
C56	0.3949 (8)	0.2436 (5)	0.4393 (4)
C61	0.1529 (7)	0.3171 (4)	0.2626 (4)
C62	0.1759 (7)	0.3883 (5)	0.2748 (4)
C63	0.1000 (9)	0.4393 (5)	0.2415 (5)
C64	0.0019 (9)	0.4196 (6)	0.1931 (5)
C65	−0.0217 (8)	0.3499 (5)	0.1781 (5)
C66	0.0533 (8)	0.2999 (5)	0.2123 (5)
C71	0.2451 (8)	0.3332 (5)	0.0867 (4)
C72	0.1953 (8)	0.3417 (5)	0.0172 (4)
C73	0.1630 (9)	0.4068 (6)	−0.0101 (5)
C74	0.1807 (7)	0.4636 (5)	0.0323 (5)
C75	0.3210 (8)	0.4575 (5)	0.1030 (4)
C76	0.2607 (8)	0.3904 (5)	0.1296 (4)
C81	0.5526 (7)	0.4080 (4)	0.3845 (4)
C82	0.5518 (8)	0.4756 (4)	0.4079 (4)
C83	0.6144 (8)	0.4932 (5)	0.4729 (5)
C84	0.6807 (7)	0.4437 (5)	0.5148 (4)
C85	0.6830 (9)	0.3763 (5)	0.4915 (5)
C86	0.6191 (9)	0.3591 (5)	0.4270 (5)

consistent with these six-coordinate species having even less freedom in the equatorial plane than their five-coordinate precursor. The structurally characterized rhenium complex $[ReBr_2(PPh_3)_2(NNPh)(NNHPh)]$ shows the conformation analogous to conformation V depicted in Figure 4.[8]

^{99}Tc NMR Spectra. Technetium-99 NMR spectroscopy is proving to be a useful technique for characterization of coordination complexes of technetium. The chemical shifts for a large number of technetium complexes have recently been reported,[21] and as is observed for all other measured nuclei,[22] a correlation between chemical shift and oxidation state has emerged. Since diazenido ligands are noninnocent and even with structural data the assignment of oxidation states in complexes with these ligands is inherently ambiguous, the ^{99}Tc NMR spectra of complexes **2**, **4**, and **5** were measured.

The crystallographic details presented in the following section establish a formal oxidation state of −1 for the five-coordinate, bis(aryldiazenido) complexes. The formal oxidation states of the singly and doubly protonated species are less obvious, especially without structural data to confirm the ligand geometries. If the singly protonated technetium complex is analogous to the structurally characterized singly protonated rhenium complex,[8] a formal oxidation state of +1 is observed. Finally, the addition of the second proton to the same ligand, without altering its geometry, is accompanied by the generation of a positive charge on the overall complex while the metal maintains a formal oxidation state of +1 (see Figure 5).

The spectrum of the five-coordinate complex **2** shows a broad singlet at 470 ppm (line width = 9000 Hz) relative to $[TcO_4]^-$ while the singly protonated complex **4** resonates at 940 ppm (line width = 9000 Hz). A similar signal was detected at 910 ppm for the doubly protonated complex **5** (line width = 9000 Hz). These values follow the established trend[21] in that the signal for complex **2**, which has the lower formal oxidation state (−1), is found upfield from complexes **4** and **5**, which have formal oxidation states of +1. Furthermore, the metal centers in complexes **4** and **5** should be in similar environments and this is reflected in their nearly superimposable ^{99}Tc NMR spectra. However, the chemical shifts for all three complexes do not fall into the regions previously established for complexes containing Tc in such low oxidation states and are closer to the region assigned to Tc(V) complexes. This implies that the metals in these complexes have a higher effective oxidation state than the formal oxidation state suggests.

Crystallography. The crystal data and experimental details of the structure determination are given in Table II. A list of atomic positional parameters for complex **1** are given in Table III.

The structural features of **1** are similar to those reported for the analogous rhenium complex.[10] The coordination sphere consists of mutually trans triphenylphosphine ligands, and the chloride and aryldiazenido ligands in the remaining three equatorial positions of the trigonal bipyramid.

---

(21) O'Connell, L. A.; Thornback, J. R.; Pearlstein, R. M.; Jones, A. G.; Davison, A. *Inorg. Chim. Acta*, in press.

(22) Jameson, C. J.; Mason, J. In *Multinuclear NMR*; Mason, J., Ed.; Plenum Press: New York, 1987; p 66.

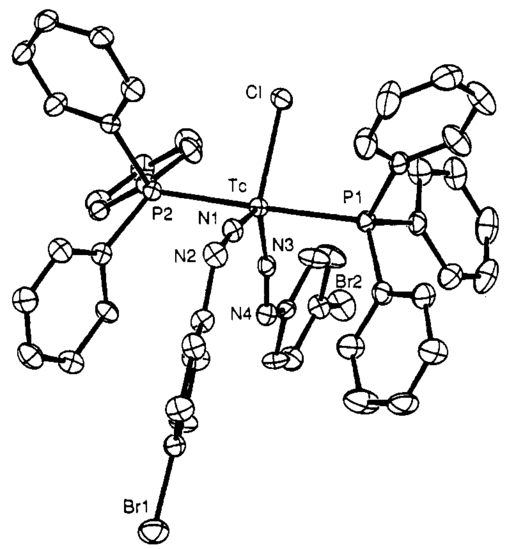


Figure 6. ORTEP diagram showing molecular structure of [TcCl(PPh$_3$)$_2$(C$_6$H$_4$Br)$_2$] with the relevant atoms labeled and 25% probability ellipsoids.

Table IV. Selected Bond Lengths (Å) and Angles (deg) for **1**

Bond Lengths			
Tc1-N1	1.796 (6)	Tc1-N3	1.783 (7)
Tc1-P1	2.438 (2)	Tc1-P2	2.445 (2)
Tc1-Cl1	2.423 (2)	N1-N2	1.229 (9)
N3-N4	1.224 (8)		
Bond Angles			
Tc1-N1-N2	170.7 (7)	Tc1-N3-N4	166.2 (6)
Cl1-Tc1-N1	118.1 (2)	Cl1-Tc1-N3	123.5 (2)
N1-Tc1-N3	118.4 (3)	P1-Tc1-P2	175.78 (7)
P1-Tc1-N1	91.7 (2)	P1-Tc1-N3	90.1 (2)
P1-Tc1-Cl1	87.14 (8)	P2-Tc1-Cl1	90.68 (8)
P2-Tc1-N1	92.5 (2)	P2-Tc1-N3	88.1 (2)
N1-N2-C71	119.7 (7)	N3-N4-C81	117.0 (7)

The aryldiazenido units display nearly linear M-N-N linkages and bond lengths reflecting multiple bonding throughout both units. The ORTEP diagram of complex **1** is shown in Figure 6, with selected atoms labeled. "Singly bent" organodiazenido units serve formally as monocationic, 2-electron-donating ligands, under the same rationale where linear nitrosyl units are considered +1 ligands.[23] The short Tc-N bonds of complex **1** suggest that significant metal-to-ligand back-bonding is present. The bond angles of the N=N—C units of 117.0 and 119.7° reflect the appropriate sp^2 hybridization for the β-nitrogen of the aryldiazenido ligands. Table IV lists selected bond lengths and angles for complex **1**. The only significant structural difference between the rhenium and technetium complexes is in the bonding parameters for the aryldiazenido units. In the technetium species, the two aryldiazenido units show nearly equivalent bonding parameters, while those in the rhenium complex differ significantly. The rhenium complex shows one long Re–N bond and the other short, 1.798 (19) and 1.726 (24) Å, as compared to 1.796 (6) and 1.783 (7) Å for the technetium complex. The N-N bond lengths of the rhenium complex are 1.241 (29) and 1.315 (36) Å, while those for the technetium species are 1.229 (9) and 1.224 (8) Å.

Table V. Least Squares Plane[a]

atoms defining plane	dist, Å	esd	atoms defining plane	dist, Å	esd
Tc1	0.0032	0.0006	C73	0.3056	0.0092
Cl1	−0.0466	0.0020	C74	0.0478	0.0080
Br1	−0.0067	0.0011	C75	−0.2193	0.0084
Br2	−0.0011	0.0010	C76	−0.2424	0.0083
N1	0.0075	0.0058	C81	0.0863	0.0070
N2	0.0351	0.0064	C82	−0.1480	0.0077
N3	0.0682	0.0057	C83	−0.1917	0.0084
N4	0.0808	0.0062	C84	0.0352	0.0077
C71	0.0468	0.0077	C85	0.2876	0.0089
C72	0.3070	0.0081	C86	0.3102	0.0088

[a] The mean deviation from the plane is 0.1239 Å.

The bond angles about the technetium show little deviation from an ideal trigonal bipyramid. The P1-Tc-P2 bond angle is 175.78(7)°. The bond angles within the equatorial plane are Cl-Tc-N1 = 118.1 (2)°; Cl-Tc-N3 = 123.5 (2)°, and N1-Tc-N3, 118.4 (3)°. The technetium, chlorine, and two (*p*-bromophenyl)diazenido ligands are essentially coplanar. The mean deviation from this plane including phenyl rings and the bromo substituents is 0.1239 Å. A slight tilt to the two phenyl rings is observed. The individual deviations from the least-squares plane are listed in Table V.

Summary. The organohydrazine chemistry presented within for technetium closely parallels the established rhenium chemistry, which has been shown to be extensive. The functional diversity of the organohydrazine ligand and its robust coordination chemistry holds promise for its utilization in the synthesis of new technetium complexes for use in diagnostic nuclear medicine.

Acknowledgment. We thank Dr. William M. Davis for his assistance with the crystallography, Dr. Catherine E. Costello and Cheng-hui Zeng for the mass spectra, and Professor Jon A. Zubieta for the samples of substituted phenylhydrazines.

Registry No. **1**, 122489-66-1; **2**, 122489-67-2; **3**, 122489-68-3; **4**, 122489-69-4; **5**, 122489-70-7; **6**, 122489-71-8; ^{99}TcCl$_4$(PPh$_3$)$_2$, 111821-29-5.

Supplementary Material Available: Listings of final positional parameters and B(eq) values for [TcCl(PPh$_3$)$_2$(NNC$_6$H$_4$Br)$_2$] including the hydrogen atoms (Table SI), anisotropic thermal parameters for [TcCl(PPh$_3$)$_2$(NNC$_6$H$_4$Br)$_2$] (Table SII), intramolecular bond lengths involving non-hydrogen and hydrogen atoms for [TcCl(PPh$_3$)$_2$(NNC$_6$H$_4$Br)$_2$] (Tables SIII and SIV), intramolecular bond angles involving non-hydrogen and hydrogen atoms (Tables SV and SVI), and complete X-ray data collection parameters for [TcCl(PPh$_3$)$_2$(NNC$_6$H$_4$Br)$_2$] (Table SVIII) (20 pages); a listing of final observed and calculated structure factors for [TcCl(PPh$_3$)$_2$(NNC$_6$H$_4$Br)$_2$] (Table SVII) (28 pages). Ordering information is given on any current masthead page.

---

[23] Enemark, J. H.; Feltham, R. D. *Coord. Chem. Rev.* **1974**, *13*, 339.