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Synthesis and Characterization of Rhenium(III) and Technetium(III) Organohydrazide Chelate Complexes. Reactions of 2-Hydrazinopyridine with Complexes of Rhenium and Technetium

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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 ^{1}H 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, $\alpha = 105.9050(10)°$, $\beta = 95.8930(10)°$, $\gamma = 111.0100(10)°$, $V = 1906.1(2)$ Å^3, $Z = 2$, and $R = 0.0650$ based on 5268 unique reflections. The FABMS+ in (*p*-nitrobenzyl alcohol) of **3** reveals a parent ion peak at *m/z* 799.2. 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 ^{1}H 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.

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. We report here a new form, the unprotonated chelate, diazenido(1−). (See Figure 1.)

Experimental Section

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 $^{31}P\{^1H\}$ 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. $^{31}P\{^1H\}$ chemical shifts are reported relative to an external standard of 85% H_3PO_4. Fast atom bombardment mass spectra of samples dissolved in *p*-nitrobenzyl alcohol matrix were recorded with a Finnigan MAT 8200 mass spectrometer equipped with an Ion

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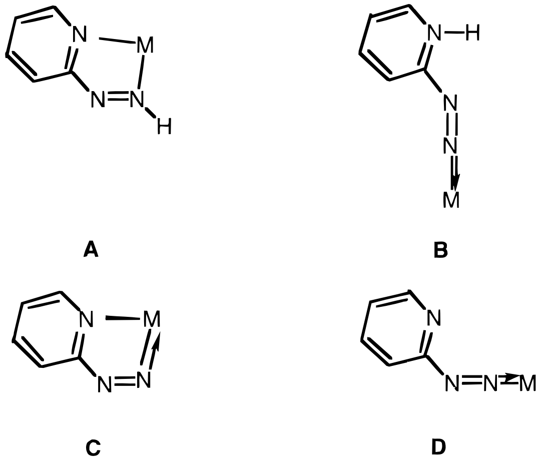

Figure 1. Neutral, organodiazene ligand (A), neutral, but zwitterionic, diazenido ligand (B), diazenido(1−) ligand (C), and terminal diazenido(1−) ligand (D).

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). Method 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 7 h. 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*-nitrobenzyl alcohol): *m/z* 887.6.

Method 2. To a 100 mL rounded bottom flask containing 0.0471 g of HYPY·2HCl in approximately 5 mL of methanol was added 0.1003 g of $Re(N)Cl_2(PPh_3)_2$ along with an additional 5 mL of methanol. The reaction mixture was heated to reflux for 1 h, 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*-nitrobenzyl alcohol). Yield: 12%.

Method 3. The same procedure as above can be followed by 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 of methanol was added 0.50 mL (3.5 mmol) of PMe_2Ph. Additional methanol was added, and the reaction mixture was stirred for 2 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 counterion in the lattice.

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	0.710 73 Å, Mo Kα	0.710 73 Å, Mo Kα
cryst system	triclinic	orthorhombic
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, deg	105.9050(10)	90
β, deg	95.8930(10)	90
γ, deg	111.0100(10)	90
V, $Å^3$	1906.1(2)	2913.9(10)
Z	2	4
D(calc), g/cm^3	1.571	1.700
abs coeff, mm^{-1}	3.322	4.490
unique data	5268	3083
R	0.0496	0.0281
$R(F^2)$	0.0650	0.0384
R_w	0.1713	0.0840

Table 2. Selected Atomic Coordinates (×10^4) for **1**

	x	*y*	*z*
Re	2864(1)	2046(1)	2222(1)
Cl(1)	5051(3)	1908(3)	2512(2)
Cl(2)	1789(3)	125(2)	1088(2)
P(1)	3818(2)	3222(2)	1296(2)
P(2)	2132(3)	941(2)	3233(2)
N(1)	2889(8)	3435(7)	2977(5)
N(2)	2037(9)	3909(9)	3162(5)
N(3)	879(8)	2182(7)	1947(5)
C(1)	813(10)	3170(8)	2545(6)
C(3)	−1406(11)	1736(12)	1214(7)
C(4)	−1491(12)	2679(13)	1847(8)
C(5)	−354(12)	3428(12)	2516(8)
C(6)	−230(10)	1501(10)	1283(6)

^1H 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*-nitrobenzyl alcohol): *m/z* 711.4.

Preparation of $Tc(NNpy)(PPh_3)_2Cl_2$ (3). A 50 mL rounded bottom flask containing 0.09967 g (0.1294 mmol) of $Tc(MeCN)(PPh_3)_2Cl_3$, 0.07372 g (0.09563 mmol) of HYPY·2HCl, and 25 mL of MeOH was refluxed for 6 h. 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. ^1H 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*-nitrobenzyl alcohol): *m/z* 799.2.

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 (λ = 0.710 73 Å). The data for **1** were collected using a crystal having dimensions 0.2 × 0.08 × 0.08 mm. The crystal system was triclinic, a = 10.5549(7) Å, b = 12.2699(8) Å, c = 16.8206(12) Å, α = 105.9050(10)°, β = 95.8930(10)°, and 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 1.29−23.34° with limiting indices $-11 \le h \le 10$, $-12 \le k \le 13$, $-16 \le l \le 18$. Of the 7684 reflections collected, 5273 were independent (R_{int} = 0.0920). The

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Table 3. Selected Atomic Coordinates ($\times 10^4$) for **2**

	x	*y*	*z*
Re	1645(1)	1439(1)	2518(1)
Cl(1)	2414(2)	1704(2)	870(2)
P(1)	758(2)	610(2)	1265(2)
P(2)	2648(2)	2313(2)	3534(3)
N(11)	1031(4)	2478(5)	2528(11)
N(12)	564(4)	3124(5)	2636(11)
N(13)	13(5)	4553(6)	2100(9)
N(21)	2218(4)	84(5)	2817(6)
N(22)	1238(5)	936(5)	3914(8)
N(23)	1436(6)	126(6)	4399(8)
C(111)	542(6)	3879(7)	1827(10)
C(112)	987(7)	3918(8)	910(11)
C(113)	893(8)	4672(8)	186(12)
C(114)	363(7)	5349(8)	395(14)
C(115)	−33(7)	5284(9)	1367(16)
C(211)	1971(5)	−358(7)	3757(9)
C(212)	2241(6)	−1258(7)	4082(12)
C(213)	2746(6)	−1709(8)	3436(12)
C(214)	3004(6)	−1273(6)	2462(21)
C(215)	2750(5)	−376(7)	2194(9)

Table 4. Selected Bond Lengths (Å) and Selected Bond Angles in (deg) of **1**

Re−N(1)	1.815(8)	N(1)−Re−N(3)	69.9(3)
Re−N(3)	2.174(8)	N(1)−Re−Cl(2)	154.3(3)
Re−Cl(1)	2.385(2)	N(3)−Re−Cl(2)	84.6(2)
Re−Cl(2)	2.378(2)	N(1)−Re−Cl(1)	110.1(3)
Re−P(1)	2.457(2)	N(3)−Re−Cl(1)	179.3(2)
Re−P(2)	2.472(2)	Cl(2)−Re−Cl(1)	95.40(9)
N(1)−N(2)	1.256(12)	N(1)−Re−P(1)	90.3(2)
N(2)−C(1)	1.391(14)	N(1)−Re−P(2)	88.9(2)
C(1)−N(3)	1.375(12)	N(3)−Re−P(1)	91.7(2)
		N(3)−Re−P(2)	93.1(2)

Table 5. Selected Bond Lengths (Å) and Selected Bond Angles in (deg) of **2**

Re−N(11)	1.802(7)	N(12)−N(11)−Re	172.0(9)
Re−N(21)	2.167(7)	N(23)−N(22)−Re	126.4(7)
Re−N(22)	1.949(9)	N(11)−Re−N(22)	94.0(4)
Re−P(1)	2.445(3)	N(11)−Re−N(21)	166.9(4)
Re−P(2)	2.453(3)	N(22)−Re−N(21)	73.2(3)
Re−Cl(1)	2.416(3)	N(11)−Re−Cl(1)	102.1(4)
N(11)−N(12)	1.221(9)	N(22)−Re−Cl(1)	163.7(2)
N(22)−N(23)	1.319(11)	N(21)−Re−Cl(1)	90.8(2)
N(23)−C(211)	1.384(13)	N(11)−Re−P(1)	90.7(3)
C(211)−N(21)	1.356(13)	N(22)−Re−P(1)	97.4(3)
N(12)−C(111)	1.43(2)	N(21)−Re−P(1)	88.7(2)
		N(11)−Re−P(2)	91.0(3)
		N(22)−Re−P(2)	90.6(3)
		N(21)−Re−P(2)	91.5(2)

structure was solved by direct methods (SHELXTL v. 5.0, G. M. Sheldrick 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 × 0.32 × 0.30 mm. The crystal system was orthorhombic, $a = 17.383(4)$ Å, $b = 13.967(3)$ Å, $c = 12.002(2)$ Å, $\alpha = \beta = \gamma = 90°$, 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 $\rho = 1.700$ g/cm^3, and $F(000) = 1468$. The data were obtained at 296(2) K in the θ range 1.87−23.27° with limiting indices $-18 \le h \le 19$, $-14 \le k \le 15$, $-6 \le l \le 13$. Of the 11 285 reflections collected, 3083 were independent ($R_{\text{int}} = 0.0448$). The structure was solved by the Patterson method (SHELXTL v. 5.0, G. M. Sheldrick 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 $I > 2\sigma(I)$.

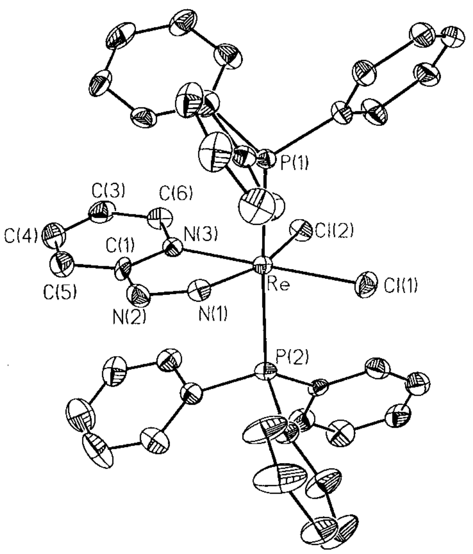

Figure 2. ORTEP of **1** with 35% ellipsoids.

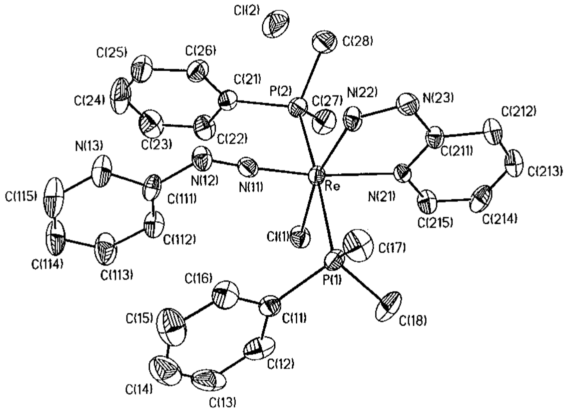

Figure 3. ORTEP of **2** with 35% ellipsoids.

Results and Discussion

Organohydrazines can react with group VII metal−oxo complexes to form metal−nitrido complexes or metal−imido complexes;[23−25] however, the organohydrazine 2-hydrazinopyridine reacts differently. In particular, 2-hydrazinopyridine has an additional mode of binding[14,26] 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 binding mode 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

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Table 6. Comparison of Bond Lengths and Angles of Organodiazenido and Organodiazene Ligands in Complexes of Rhenium and Technetium

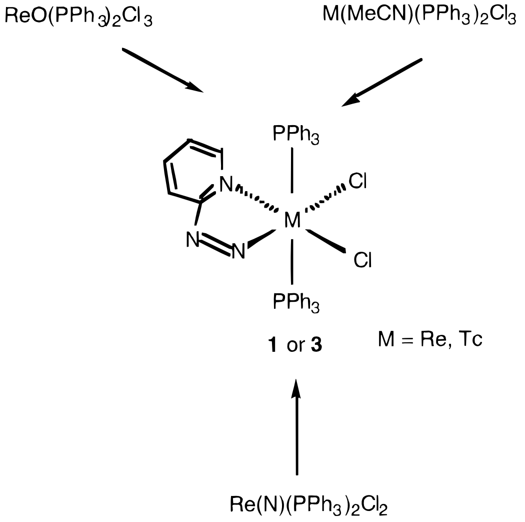
complex	M−N (Å)	N−N (Å)	M−N−N (deg)	N−N−C (deg)
$Tc(C_8H_5N_4)Cl_2(PPh_3)_2$[15]	1.767(12)	1.274(17)	138.6(7)	104.9(11)
	2.151(9)			
$Re(hydralazine)Cl_2(PPh_3)_2$[26]	1.79(2)	1.29(2)	136.4(9)	106.0(14)
	2.14(2)			
$Re(NNpy)(PPh_3)_2Cl_2$ (**1**)	1.815(8)	1.256(12)	137.3(7)	105.8(8)
	2.174(8)			
$Re(HNNpy)(NNpyH)Cl_3$[22]	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)
$Re(HNNpy)(NNpy)Cl_2(PPh_3)$[28]	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)
$[Re(HNNpy)(NNpy)(PMe_2Ph)_2Cl]^+$ (**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)

as a diamagnetic pseudo-M(I) complex. This diamagnetic behavior is seen in the ^1H NMR spectra of these d^4 octahedral complexes. For complexes **1**−**3**, the sharp pyridyl proton resonances are seen in the 6−8 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 to −17.88 ppm.[27] 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.[22,28]

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 a Re−N(1) bond length of 1.815(8) Å, a N(1)−N(2) bond length of 1.256(12) Å, and a Re−N(3) 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-N(22) bond length of 1.949(9) Å, a N(22)−N(23) bond length of 1.319(11) Å, and a Re−N(21) bond length of 2.167(7) Å. Evidence for a hydrogen bound to the α-nitrogen (N(22)) is found in the ^1H 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 N(11)−N(12) bond length of 1.221(9) Å and a short Re−N(11) 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−N(11)−N(12) bond angle of 172.0(9)°, which makes it unlikely that the resonance found at 19 ppm in the ^1H NMR is due to a hydrogen bound to N(11).

Scheme 1



As shown in Table 6, the bond lengths and angles of complex **1** are very similar to the rhenium[26] 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

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(27) Breikss, A. I. Ph.D. Thesis, Massachusetts Institute of Technology, 1989.

(28) Nicholson, T. L.; Cook, J.; Davison, A.; Zubieta, J. A.; Jones, A. G. *Inorg. Chim. Acta* **1996**, *252*, 427.

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 organohydrazine 2-hydrazinopyridine reacts with rhenium(V), rhenium(III), and technetium(III) synthons to form metal−organohydrazide complexes. The organohydrazide 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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Supporting Information Available: For compounds **1** and **2**, tables providing complete information on the crystallographic data collection, final values of all refined atomic coordinates, calculated positions of hydrogen atoms, thermal parameters, and all bond lengths and angles (15 pages). Ordering information is given on any current masthead page.

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