Synthesis and Characterization of Rhenium(III) Organohydrazide Compounds. Crystal and Molecular Structures of [ReCl(PPh₃)₂(NHNC₅H₄N)(HNNC₅H₄N)]Cl₂, [Re{2-(Ph₂P)C₆H₄S}{2-(Ph₂PO)C₆H₄S}(NNC₅H₄N)(HNNC₅H₄N)], and [Re{2-(Ph₂P)C₆H₄S}₂(NNC₅H₄N)]

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The reduction of ReO_4^- with 2-hydrazinopyridine dihydrochloride and PPh_3 gives [ReCl(PPh₃)₂(NHNC₅H₄N)-(HNNC₅H₄N)]Cl₂ (**2**). A similar reaction using 2-hydrazino-2-imidazoline and PPh_3 in methanol hydrochloric acid allows the preparation of [ReCl₃(PPh₃)₂(NNC₃H₄N₂)] (**3**). The reaction of the Re(III) complex [ReCl₃(NNC₅H₄-NH)(HNNC₅H₄N)] (**1**), with 2-(Ph₂P)C₆H₄SH in methanol yields [Re{2-(Ph₂P)C₆H₄S}{2-(Ph₂PO)C₆H₄S}-(NNC₅H₄N)(HNNC₅H₄N)] (**4**) and [Re{2-(Ph₂P)C₆H₄S}₂(NNC₅H₄N)] (**5**). The same precursor with 2-(Ph₂PO)-6-(Me₃Si)C₆H₃SH gives [ReCl{2-(Ph₂PO)-6-(Me₃Si)C₆H₃S}(NNC₅H₄N)(HNNC₅H₄N)] (**6**) and with PhP(C₆H₄SH-2)₂ yields [Re{PhP(C₆H₄S-2)₂}(NNC₅H₄N)(HNNC₅H₄N)] (**7**). Crystal data: **2**, C₄₆H₃₉N₆P₂Cl₃Re, orthorhombic, *Pnma*, a = 19.6381(7) Å, b = 15.1861(6) Å, c = 15.0711(5) Å, V = 4494.6(3) Å³, Z = 6, 5646 reflections, R = 0.0655; **4**, C₄₆H₃₇N₆OP S₂Re, triclinic, $P\bar{1}$, a = 9.4233(2) Å, b = 15.8308(3) Å, c = 16.3530(2) Å, α = 61.88(10)°, β = 80.9220(10)°, γ = 85.1350(10)°, V = 2124.40(7) Å³, Z = 2, 8728 reflections, R = 0.0757; **5**, monoclinic, $P2_1/c$, a = 10.0006(2) Å, b = 18.1857(1) Å, c = 19.8595(2) Å, β = 94.09(1)°, V = 3598.08(8) Å³, Z = 4, 8406 reflections, R = 0.0359.

Introduction

The continued elaboration of the chemistry of the group VII congeners technetium and rhenium reflects the use of their radionuclides either as diagnostic imaging agents (⁹⁹ᵐTc) or as therapeutic radiopharmaceuticals (¹⁸⁶,¹⁸⁸Re).[1−23] The radionu-

clides of Re are β-emitters with properties which make them suitable candidates for therapeutic applications. Rhenium-186 is particularly attractive[17−19] because of its half-life (90 h) and strong β-emission (β_{max} 1070 keV) capable of delivering high radiation doses to tissues. Rhenium-188, also a β-emitting radionuclide (β_{max} 2120 keV), having a half-life of 17 h and available from a ¹⁸⁸W/¹⁸⁸Re radionuclide generator at no carrier added levels,[20] has become the logical choice for the development of radiopharmaceuticals for use in the treatment of cancer.[21] In addition, the rhenium isotopes possess the advantage of a photon emission at approximately the same energy as that of ⁹⁹ᵐTc, making it possible to monitor the biodistributions of rhenium radiopharmaceuticals with the same equipment employed for the ⁹⁹ᵐTc agents.[22]

The periodic relationship between technetium and rhenium suggests that therapeutic Re radiopharmaceuticals can be designed by analogy to existing ⁹⁹ᵐTc diagnostic agents. Thus,

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Scheme 1
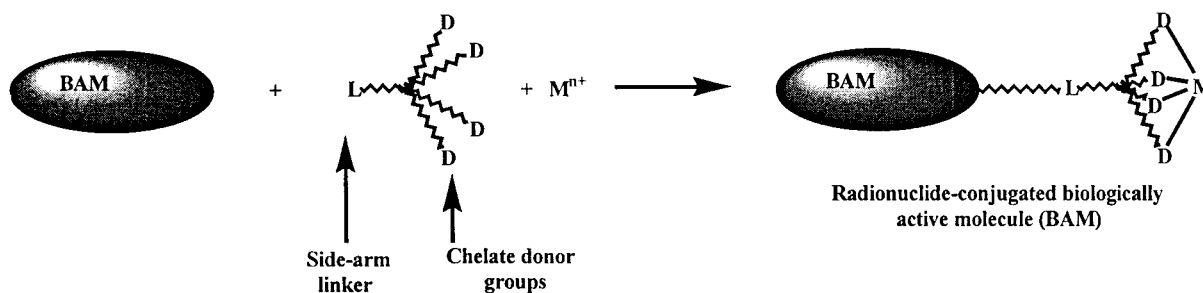
it is anticipated that ^{99m}Tc radiodiagnostic agents which accumulate in abnormal tissue may be used to model the development of ^{186,188}Re analogues with similar biodistribution patterns.[23] The site-specific Re analogue will deliver a therapeutically significant radiation dose without affecting normal tissue.

Radiopharmaceuticals may be classified into two broad categories: (1) those having biological distributions determined strictly by blood flow, or perfusion, and targeting high-capacity systems such as glomerular filtration, phagocytosis, hepatocyte clearance, and bone absorption[24−27] and (2) those whose distribution is determined by specific enzymatic or receptor binding interactions and which target low-capacity sites.[1−4,28−30] An effective strategy for linking radioactive metal cations to biologically active molecules (BAM) is the bifunctional chelate approach.[31] For example, the construction of effective radio-immunoconjugates requires selection of an appropriate metal radionuclide and organic chelating agent combination, along with the strategy and conditions for assembling the metal-chelating agent−antibody complex. The bifunctional ligand serves two purposes: to hold the metal radionuclide securely

without leakage in vivo and to provide a sidearm for antibody linkage while maintaining maximum antibody integrity. The construction of a radionuclide-conjugated BAM from its component units is illustrated diagramatically in the Scheme 1.

While numerous examples of labeled conjugates have been investigated, improved bifunctional ligands for efficient and stable incorporation of radiometallic nuclides under mild conditions must be developed to overcome the significant problems often associated with this technology, such as nonspecific binding of the radionuclide, protein denaturation under the conditions required for chelation of the metal, and slow kinetics of radionuclide labeling. Our original efforts in technetium coordination chemistry were directed toward this end and resulted in the development of a series of bifunctional hydrazine ligands which have proved effective and versatile linkers for labeling antibodies and fragments,[32] somatostatin analogues, antisense oligonucleotides, and a cyclic GPIIb/IIIa receptor antagonist.[34] Specifically, when *N*-oxysuccinimidyl-hydrazinonicotinamide is combined with a macromolecule such as a protein, polypeptide, or glycoprotein in neutral or slightly basic media, the protein-reactive part of the compound reacts with nucleophilic groups in the macromolecule, such as the amine groups of lysine residues, to yield a conjugate containing free hydrazine/hydrazide groups, referred to as an HYNIC-protein (Scheme 2).

The hydrazine unit acts as an effective ligating group for metal cations[35] which are incorporated into the conjugate to yield the labeled macromolecule. The versatility of the linker technol-

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Scheme 2
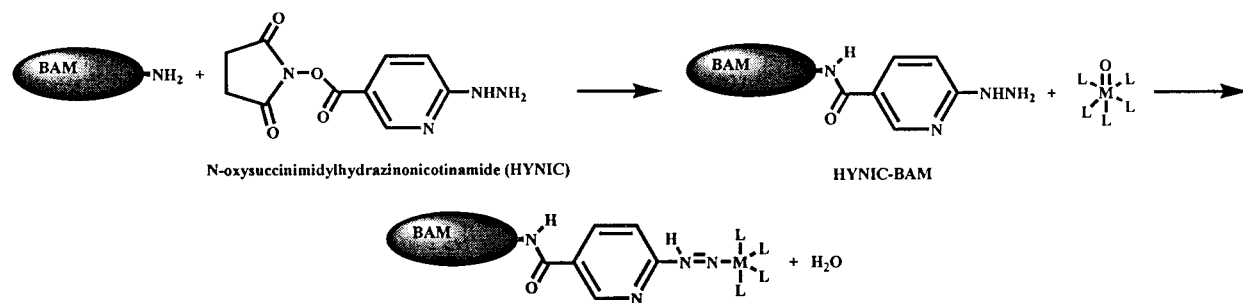
ogy in related applications, such as the synthesis of conjugates of chemotactic peptides, has led to natural products which bind to high-affinity receptors on white blood cell membranes and thereby migrate to sites of infection.[36-38] However, despite the manifest potential of bifunctional organohydrazino ligands in protein radiolabeling for nuclear medicinal applications, the chemistry of the metal coordination to the HYNIC linker was only recently structurally defined.[39] To explore the structural possibilities for the coordination chemistry relevant to these reagents, we investigated the chemistry of Tc and Re with hydrazinopyridine, which not only established the formation of the robust {M≡NNR} core but also implicated chelate formation through the pyridine nitrogen as a significant structural determinant.

During the course of these studies, we also noted that the identity of the coligands coordinated to the metal site may profoundly influence the structures of complexes with the metal–hydrazido core, {MNNR}, and the radiochemical yield of the protein conjugate. Sulfur ligands were particularly effective in the stabilization of the metal–hydrazido core as a consequence of the high affinity of Tc and Re for sulfur donors. As part of this continuing investigation of the effect of various coligand types on the structural chemistry and stability of the {MNNR} core, Re–hydrazido complexes with phosphorus donor and mixed phosphorus–sulfur donor ligands have been investigated. The chemistry and structures of the complexes [ReCl-(PPh$_3$)$_2$(NHNC$_5$H$_4$N)(HNNC$_5$H$_4$N)]Cl$_2$ (**2**), [ReCl$_3$(PPh$_3$)$_2$-(NNC$_3$H$_4$N$_2$)] (**3**), [Re{2-(Ph$_2$P)C$_6$H$_4$S}{2-(Ph$_2$PO)C$_6$H$_4$S}-(NNC$_6$H$_4$N)(HNNC$_5$H$_4$N)] (**4**), [Re{2-(Ph$_2$P)C$_6$H$_4$S}$_2$(NNC$_5$H$_4$N)] (**5**), [ReCl{2-(Ph$_2$PO)-6-(SiMe$_3$)C$_6$H$_3$S}(NNC$_5$H$_4$N)(HNNC$_5$H$_4$N)] (**6**), and [Re{PhP(C$_6$H$_4$S-2)$_2$}(NNC$_5$H$_4$N)(HNNC$_5$H$_4$N)] (**7**) are discussed.

Experimental Section

General Information. All manipulations were carried out under an inert atmosphere of dry nitrogen. Ammonium perrhenate, 2-hydrazino-2-imidazoline, 2-hydrazinopyridine dihydrochloride, PPh$_3$, and NEt$_3$ were purchased from Aldrich and used without further purification. Syntheses of the phosphino thiol ligands were carried out using slight modifications of the standard literature procedure involving lithiation of benzenethiol.[40] The precursor [ReCl$_3$(NNC$_5$H$_4$NH)(HNNC$_5$H$_4$N)] (**1**) was prepared by the reduction of sodium perrhenate with 2-hydrazi-

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nopyridine dihydrochloride.[41] Elemental analyses were performed on a Carlo-Erba EA microanalyzer. IR spectra were recorded in KBr disks using a Bruker IFS 66v spectrophotometer. ^{1}H and ^{31}P NMR spectra were recorded on a Bruker WM 300 MHz instrument using CDCl$_3$ as solvent. ^{1}H NMR chemical shifts were determined against TMS as internal standard. ^{31}P NMR chemical shifts were determined against 85% H$_3$PO$_4$. The FAB mass spectra were recorded on a Kratos MS50TC spectrometer, using 3-nitrobenzyl alcohol (3-NOBA) as a matrix.

Preparation of [ReCl(PPh$_3$)$_2$(NHNC$_5$H$_4$N)(HNNC$_5$H$_4$N)]Cl$_2$ (2).
Method 1. To a refluxing solution of NH$_4$ReO$_4$ (0.500 g, 1.860 mmol) and 37% HCl (0.276 g, 7.460 mmol) in 25 mL of methanol was added 2-hydrazinopyridine dihydrochloride (1.340 g, 7.460 mmol). The mixture was stirred briefly at room temperature and refluxed with stirring for 3 h. The reaction mixture was filtered, and the filtrate was treated with 4 equiv of triphenylphosphine (1.950 g, 7.460 mmol) and 4 equiv of NEt$_3$ (0.753 g, 7.460 mmol). This mixture was refluxed for 1 h, followed by filtration, and the filtrate was evaporated in vacuo to dryness. Crystals of **2** were grown by slow diffusion of hexane into a CH$_2$Cl$_2$ solution of the residue. The yield of crystalline material was approximately 35%.

Method 2. A solution of [ReCl$_3$(HNNC$_5$H$_4$N)(NNC$_5$H$_4$NH)] (0.05 g, 0.098 mmol) with triphenylphosphine (0.103 g, 0.394 mmol) and NEt$_3$ (0.040 g, 0.394 mmol) in 15 mL of methanol was stirred and refluxed for 1 h. The dark red reaction mixture was evaporated to dryness under vacuum. Dark red crystals were grown by slow diffusion of pentane into a CH$_2$Cl$_2$ solution of **2** (0.030 g, 31%). Anal. Calcd for C$_{46}$H$_{40}$Cl$_3$N$_6$P$_2$Re (mol wt 1032.56): C, 53.5; H, 3.87; N, 8.14. Found: C, 53.4; H, 3.85; N, 8.00. IR (KBr, cm^{-1}) 1542 (m), 1422 (s), 1294 (m), 1049 (w), 746 (m), 695 (s). ^{1}H NMR (CD$_2$Cl$_2$, ppm): 6.5–8.5 (mm). ^{31}P NMR (CD$_2$Cl$_2$, ppm): 8.75 (s).

Preparation of [ReCl$_3$(PPh$_3$)$_2$(NNC$_3$H$_4$N$_2$)] (3). To a refluxing solution of NH$_4$ReO$_4$ (0.050 g, 0.186 mmol), 10 mL of ethanol, and 1 mL of 37% HCl was added a solution of triphenylphosphine (0.122 g, 0.466 mmol), 1 mL of ethanol, and 2-hydrazino-2-imidazoline. The mixture was stirred and refluxed for 0.5 h, after which it was filtered and the blue-green precipitate was allowed to air-dry (yield 0.052 g, 30%). Anal. Calcd for C$_{39}$H$_{34}$Cl$_3$N$_4$P$_2$Re (mol wt 913): C, 51.17; H, 3.38; N, 6.12. Found: C, 50.74; H, 4.07; N, 5.98. IR (KBr, cm^{-1}): 3246 (w), 1580 (s), 1553 (m), 1482 (m), 1434 (s), l347 (s), 1290 (m), 1189 (m), 1158 (w), 1093 (s), 1028 (w), 998 (m), 926 (w), 746 (s), 695 (s), 594 (m), 520 (s).

Preparation of [Re{2-(Ph$_2$P)C$_6$H$_4$S}{2-(Ph$_2$PO)C$_6$H$_4$S}(NNC$_5$H$_4$N)-(HNNC$_5$H$_4$N)] (4) and [Re{2-(Ph$_2$P)C$_6$H$_4$S}$_2$(NNC$_5$H$_4$N)] (5). To a refluxing solution of 2-(Ph$_2$P)C$_6$H$_4$SH (0.200 g, 0.680 mmol) in 50 mL of methanol was added a solution of [ReCl$_3$(NNC$_5$H$_4$NH)-(HNNC$_5$H$_4$N)] (0.135 g, 0.270 mmol) in 15 mL of methanol. Subsequently, NEt$_3$ (0.068 g, 0.700 mmol) was added to this solution. The solution was stirred at room temperature for 2 days, whereupon the reaction mixture was filtered and the orange-red solid was allowed to air-dry (yield 0.110 g, 46%). Crystals of **5** were grown by slow diffusion of ether into a CH$_2$Cl$_2$ solution of the precipitate. Anal. Calcd for C$_{41}$H$_{32}$N$_3$P$_2$S$_2$Re (mol wt 878.77): C, 56.02; H, 3.64; N, 4.78; S,

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7.29. Found: C, 56.08; H, 3.43; N, 4.48; S, 6.98. ^{1}H NMR (CDCl$_3$, ppm): 8.1−6.4 (mm). ^{31}P NMR (CDCl$_3$, ppm): 42.1, 41.2, 40.3, 39.3. IR (KBr, cm^{-1}): 1574 (m), 1420 (s), 1372 (s), 1286 (w), 1243 (w), 1198 (m), 1094 (m), 746 (s), 696 (s), 522 (s).

The filtrate from the isolation of **5** was taken to dryness, and crystals of **4** were grown by slow diffusion of ether into a CH$_2$Cl$_2$ solution of the residue (yield 0.108 g, 47%). Anal. Calcd for C$_{46}$H$_{37}$N$_6$P$_2$OS$_2$Re (mol wt 1001.2): C, 55.2; H, 3.70; N, 8.40; S, 6.40. Found: C, 56.0; H, 3.63; N, 8.22; S, 6.21. ^{1}H NMR (CDCl$_3$, ppm): 12.0 (1H, s), 8.8−6.3 (36H, mm). ^{31}P NMR (CDCl$_3$, ppm): 29.1, 28.3. IR (KBr, cm^{-1}): 1575 (m), 1549 (s), 1458 (m), 1421 (s), 1294 (m), 1243 (w), 1206 (w), 1098 (w), 741 (m), 695 (m), 528 (w).

Preparation of [ReCl{2-(Ph$_2$PO)-6-(Me$_3$Si)C$_6$H$_3$S}(NNC$_5$H$_4$N)-(HNNC$_5$H$_4$N)] (6). A solution of [ReCl$_3$(HNNC$_5$H$_4$N)(NNC$_5$H$_4$NH)] (0.052 g, 0.103 mmol), 2-(Ph$_2$PO)-6-(SiMe$_3$)C$_6$H$_3$SH (0.100 g, 0.262 mmol), and Et$_3$N (0.026 g, 0.27 mmol) in 40 mL of ethanol was refluxed for 12 h. A violet residue was obtained by concentration of the resulting solution. Crystals were grown by diffusion of ether into a solution of **6** in dichloromethane (yield 0.056 g, 67%). Anal. Calcd for C$_{31}$H$_{31}$-ClN$_6$POSSiRe (mol wt 815.5): C, 45.7; H, 3.68; N, 10.31; S, 3.93. Found: C, 45.2; H, 3.63; N, 10.01; S, 3.82. ^{1}H NMR (CDCl$_3$, ppm): 12.0 (1H, s), 8.6−6.2 (21H, mm), 0.3 (9H, s). ^{31}P NMR (CDCl$_3$, ppm): 47.4. IR (KBr, cm^{-1}): 1572 (m), 1550 (m), 1120 (s), 852 (s).

Preparation of [Re{PhP(C$_6$H$_4$S-2)$_2$}(NNC$_5$H$_4$N)(HNNC$_5$H$_4$N)] (7). To a refluxing solution of PhP(C$_6$H$_4$SH-2)$_2$ (0.130 g, 0.398 mmol) in 50 mL of methanol was added a solution of [ReCl$_3$(HNNC$_5$H$_4$N)-(NNC$_5$H$_4$NH)] (0.100 g, 0.198 mmol) in 15 mL of methanol. After 10 min of stirring, NEt$_3$ was added to the solution (0.073 g, 0.717 mmol). The resulting solution was refluxed for 12 h and then filtered to obtain a brown solid that was air-dried (yield 0.207 g, 72%). Anal. Calcd for C$_{28}$H$_{22}$N$_6$PS$_2$Re (mol wt 723.82): C, 46.4; H, 3.06; N, 11.61; S, 8.86. Found: C, 46.2; H, 2.92; N, 10.92; S, 8.46. ^{1}H NMR (CDCl$_3$, ppm): 15.0 (1H, s), 8.6−6.4 (21H, mm). ^{31}P NMR (CDCl$_3$, ppm): 38.2. IR (KBr, cm^{-1}): 1624 (m), 1550 (m), 1417 (s), 1107 (m), 1045 (m), 744 (s).

X-ray Crystallography. All compounds were studied on a Siemens SMART system using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). All data collections were carried out at low temperature. The crystal parameters and experimental details of the data collection are summarized in Table 1. A complete description of the details of the crystallographic methods is given in the Supporting Information. The structures were solved by direct methods.[42] Neutral atomic scattering factors were taken from Cromer and Waber,[43] and anomalous dispersion corrections were taken from Creagh and McAuley.[44] All calculations were performed using SHELXTL.[45] Non-hydrogen atoms were refined anisotropically. No anomalies were encountered in the refinements of any of the structures. Atomic positional parameters and isotropic temperature factors for the structures are presented in Tables 2−4.

Results and Discussion

Perrhenates can be reduced by organohydrazines in a hydrochloride medium to give Re(III) complexes containing organohydrazide ligands, defined generically as a ligand derived from a organohydrazine, in reactions involving a two-electron oxidation of two of the hydrazinopyridine molecules which subsequently coordinate as species with nitrogen−nitrogen double bonds. In this context, the reaction of sodium perrhenate with 2-hydrazinopyridine dihydrochloride has been shown to give the previously structurally characterized [ReCl$_3$(NNC$_5$H$_4$-NH)(HNNC$_5$H$_4$N)] (**1**) with a Re(III) center octahedrally

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(43) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974.
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Table 1. Summary of Crystal Data and Data Collection and Structure Refinement Details for [ReCl(PPh$_3$)$_2$(NHNC$_5$H$_4$N)(HNNC$_5$H$_4$N)]Cl$_2$ (**2**), [Re{2-(Ph$_2$P)C$_6$H$_4$S}{2-(PH$_2$PO)C$_6$H$_4$S}(NNC$_5$H$_4$N)(HNNC$_5$H$_4$N)] (**4**), and [Re{2-(Ph$_2$P)C$_6$H$_4$S}$_2$(NNC$_5$H$_4$N)] (**5**)

	2	**4**	**5**
empirical formula	C$_{46}$H$_{40}$N$_6$P$_2$Cl$_3$Re	C$_{46}$H$_{37}$N$_6$P$_2$S$_2$ORe	C$_{41}$H$_{32}$N$_3$P$_2$S$_2$Re
fw	1032.56	1001.20	878.77
cryst syst	orthorhombic	triclinic	monoclinic
space group	*Pnma*	*P*$\bar{1}$	*P*2$_1$/*c*
a, Å	19.6381(7)	9.4233(2)	10.0006(2)
b, Å	15.1861(6)	15.8308(3)	18.18570(10)
c, Å	15.0711(5)	16.3530(2)	19.8595(2)
α, deg		61.88(1)	
β, deg		80.922(1)	94.087(10)
γ, deg		85.135(1)	
V, Å^3	4494.6(3)	2124.40(7)	3598.08(8)
Z	4	2	4
d_{calc}, g cm^{-3}	1.526	1.565	1.622
λ, Å (Mo Kα radiation)	0.710 73	0.710 73	0.710 73
μ(Mo Kα), mm^{-1}	2.993	2.968	3.580
T, K	150	293	293
no. of reflns collected	27 182	12 733	22 466
no. of indept reflns	5646	8728	8406
F(000)	2060	692	1452
R^a	0.0656	0.0757	0.0359
$R_w{}^b$	0.1256	0.1995	0.0816

^{a} $R = \sum(|F_o| - |F_c|)/\sum|F_o|$. ^{b} $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

coordinated by three meridional chloride ligands, a neutral pyridyldiazene chelate ligand, HNNC$_5$H$_4$N, and a monodentate neutral pyridiniumyldiazenido ligand, $^-$NNC$_5$H$_4$NH$^+$.[41] Although this reaction proceeds in 90% yield, the possibility of formation of minor rhenium−pyridylhydrazino species could not be ignored. An investigation into the nature of possible minor products of the ammonium perrhenate/organohydrazine system was warranted. These considerations led us to examine the effect of adding triphenylphosphine to the filtrate of the reaction mixture which yielded **1**, a procedure which led to the production of **2**. The strategy was to add 4 equiv of triphenylphosphine to the filtrate under basic conditions. The resulting solution, after being neutralized by addition of 4 equiv of NEt$_3$ and evaporated to dryness, yielded an unusual cationic species isolated as the chloride salt, [ReCl(PPh$_3$)$_2$(η^1-NHNC$_5$H$_4$N)(η^2-HNNC$_5$H$_4$N)]-Cl$_2$ (**2**).

This observation led to the development of a second method, a two-step synthesis for the preparation of compound **2** starting from the precursor **1**. The synthesis requires the addition of 4 equiv of triphenylphosphine and 4 equiv of base to the filtrate, which is then refluxed for 1 h to produce **2** in good yield. Crystals of **2** suitable for X-ray studies were obtained by slow diffusion of hexane into a CH$_2$Cl$_2$ solution of the compound. Curiously, the metal center is formally Re(III) with two organodiazenes acting as neutral ligands and two chlorine counterions present to balance the charge. The assignment is confirmed by X-ray data supporting the presence of a neutral bidentate diazene ligand protonated on the α-nitrogen and a monodentate neutral diazene protonated on the β-nitrogen. In other examples of structures of this type, such as **1**, the proton lies on the pyridyl nitrogen atom. However the trans triphenylphosphine ligands constrain the hydrazino ligands into a planar orientation, wherein steric restraints preclude the protonation of both the α-nitrogen of the bidentate diazene and the pyridyl nitrogen of the monodentate diazene. In addition, two neutral triphenylphosphine ligands replace two chlorine atoms. The oxidation state

Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{Å}^2 \times 10^3$) for [ReCl(PPh$_3$)$_2$(NHNC$_5$H$_4$N)(HNNC$_5$H$_4$N)]Cl$_2$ (**2**)

	x	y	z	U(eq)
Re(1)	2324(1)	2500	5409(1)	35(1)
Cl(1)	1117(1)	2500	5621(2)	48(1)
Cl(2)	3236(2)	2500	9993(2)	85(1)
Cl(3)	4727(1)	2500	3529(3)	82(1)
P(1)	2170(1)	865(1)	5410(1)	41(1)
N(1)	2696(4)	2500	6483(4)	44(2)
N(2)	2919(4)	2500	7271(5)	53(2)
N(3)	4099(6)	2500	6642(8)	93(4)
N(4)	3180(4)	2500	4820(5)	41(2)
N(5)	3240(5)	2500	3981(5)	42(2)
N(6)	2086(4)	2500	3989(4)	38(2)
C(1)	3620(5)	2500	7360(7)	54(3)
C(2)	3853(5)	2500	8189(6)	50(3)
C(3)	4527(7)	2500	8374(9)	99(6)
C(4)	4997(7)	2500	7724(10)	128(8)
C(5)	4779(6)	2500	6834(9)	103(6)
C(6)	2679(5)	2500	3468(5)	37(2)
C(7)	2663(6)	2500	2541(6)	49(2)
C(8)	2032(6)	2500	2133(7)	64(3)
C(9)	1456(6)	2500	2631(6)	59(3)
C(10)	1494(5)	2500	3554(6)	44(2)
C(11)	1711(3)	425(5)	6381(4)	48(2)
C(12)	1454(4)	−423(6)	6356(5)	64(2)
C(13)	1109(4)	−758(7)	7098(7)	82(3)
C(14)	1031(5)	−257(9)	7847(7)	87(3)
C(15)	1300(5)	571(9)	7880(5)	82(3)
C(16)	1640(4)	937(7)	7144(4)	60(2)
C(17)	1672(3)	494(5)	4462(4)	47(2)
C(18)	1995(5)	281(6)	3669(5)	62(2)
C(19)	1600(6)	55(7)	2937(6)	85(3)
C(20)	913(6)	17(8)	2991(6)	92(3)
C(21)	591(5)	232(8)	3762(6)	87(3)
C(22)	961(4)	469(6)	4511(5)	61(2)
C(23)	2955(4)	218(5)	5374(4)	50(2)
C(24)	2932(5)	−679(7)	5243(7)	84(3)
C(25)	3549(7)	−1153(8)	5293(8)	109(5)
C(26)	4158(6)	−761(9)	5465(7)	97(4)
C(27)	4179(5)	109(9)	5555(7)	90(3)
C(28)	3575(4)	604(7)	5526(5)	66(2)

Table 3. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{Å}^2 \times 10^3$) for [Re{2-(Ph$_2$P)C$_6$H$_4$S}{2-(PH$_2$PO)C$_6$H$_4$S}(HNNC$_5$H$_4$N)(HNNC$_5$H$_4$N)] (**4**)

	x	y	z	U(eq)
Re(1)	3089(1)	1709(1)	2341(1)	19(1)
P(1)	3851(5)	805(4)	1482(3)	21(1)
P(2)	1716(6)	4443(4)	3694(4)	28(1)
S(1)	5594(5)	1609(4)	2497(4)	27(1)
S(2)	2990(5)	2571(3)	3262(3)	24(1)
N(1)	1091(16)	1380(12)	2578(12)	24(3)
N(2)	412(20)	604(13)	3280(13)	31(4)
N(3)	2700(18)	421(12)	3668(12)	23(3)
N(4)	2825(16)	2753(11)	1281(10)	17(3)
N(5)	2514(18)	3452(12)	539(12)	26(3)
N(6)	66(17)	3028(13)	1005(12)	26(4)
O(1)	1775(18)	5323(12)	3802(11)	38(4)
O(2)	4213(33)	5777(20)	4218(24)	95(9)
C(1)	1367(24)	95(18)	3890(14)	33(5)
C(2)	936(33)	−739(19)	4692(17)	44(6)
C(3)	1957(28)	−1257(19)	5277(19)	47(6)
C(4)	3317(32)	−934(19)	5085(16)	45(6)
C(5)	3662(27)	−99(17)	4269(15)	36(5)
C(6)	1068(20)	3585(15)	352(14)	26(4)
C(7)	828(26)	4301(16)	−527(16)	34(5)
C(8)	−638(28)	4407(18)	−704(15)	43(6)
C(9)	−1668(23)	3887(18)	−55(17)	39(6)
C(10)	−1323(22)	3197(16)	806(16)	32(5)
C(11)	5787(22)	575(15)	1490(13)	27(4)
C(12)	6526(21)	16(15)	1123(15)	27(4)
C(13)	8003(23)	−158(16)	1172(18)	37(5)
C(14)	8662(22)	199(16)	1619(18)	36(5)
C(15)	7910(23)	703(16)	2050(15)	33(5)
C(16)	6463(18)	921(13)	1981(12)	19(3)
C(17)	3580(22)	1466(15)	274(14)	26(4)
C(18)	4685(27)	1744(17)	−474(15)	38(5)
C(19)	4357(33)	2255(21)	−1363(20)	51(7)
C(20)	3031(35)	2547(19)	−1600(18)	48(7)
C(21)	1887(29)	2292(18)	−865(21)	44(6)
C(22)	2147(21)	1755(15)	56(3)	26(4)
C(23)	3077(18)	−372(14)	1906(16)	25(4)
C(24)	2345(21)	−597(16)	1342(16)	31(5)
C(25)	1756(21)	−1515(18)	1709(19)	38(5)
C(26)	1882(25)	−2190(17)	2625(19)	41(6)
C(27)	2618(22)	−1957(15)	3163(16)	33(5)
C(28)	3176(25)	−1089(15)	2796(16)	33(5)
C(29)	3524(19)	3747(15)	2541(14)	25(4)
C(30)	4549(20)	3964(15)	1746(16)	28(4)
C(31)	5064(24)	4891(18)	1170(16)	36(5)
C(32)	4592(23)	5647(14)	1375(14)	28(4)
C(33)	3568(22)	5439(16)	2154(15)	28(4)
C(34)	3013(22)	4519(15)	2713(13)	27(4)
C(35)	−102(25)	4323(21)	3467(17)	43(6)
C(36)	−386(23)	3780(15)	3067(15)	31(5)
C(37)	−1751(33)	3776(22)	2869(17)	51(7)
C(38)	−2856(25)	4298(28)	3140(20)	64(10)
C(39)	−2568(33)	4768(39)	3582(36)	97(16)
C(40)	−1174(26)	4832(24)	3727(22)	54(7)
C(41)	2134(21)	3408(15)	4719(13)	24(4)
C(42)	1161(30)	2656(25)	5325(21)	57(8)
C(43)	1534(26)	1926(22)	6109(19)	49(7)
C(44)	2909(29)	1827(19)	6341(20)	52(7)
C(45)	3909(28)	2566(26)	5730(18)	59(9)
C(46)	3480(26)	3291(19)	4979(20)	51(7)

of the rhenium atom was based on the charge requirements, close examination of the organodiazene bond lengths (vide infra), and the diamagnetic nature of the compound. The IR spectrum of this complex displays a dominant band at 745 cm^{-1} attributed to ν(Re$-$P) and peaks at 1542 and 1422 cm^{-1} assignable to ν(N$=$N) and ν(C$=$N)/ν(C$=$C) stretches. The ^{1}H NMR spectrum displays multiplet peaks in the aromatic region between δ 8.4 and 6.4 ppm and a broad signal at δ 12.0 ppm corresponding to the α-N$-$H proton. A similarly broad signal appears at ca. δ 12.0 ppm for compound **4**, which possesses only an α-N$-$H proton. In both cases, addition of D$_2$O resulted in exchange of α-N$-$H protons and disappearance of the signal. In DMF-d_7 solution, the basic nature of the DMF also resulted in exchange of the α-N$-$H proton of **1**; consequently, the signal was again unobserved.[41] The β-N$-$H signal of **2** is masked by the aromatic protons, rendering spectroscopic confirmation of the X-ray assignment unattainable. Similar difficulties were encountered previously in the spectroscopic assignments of [ReCl$_2$(PPh$_3$)$_2$(NNHCOPh)(HNNHCOPh)][46] and [ReCl$_2$(NH$_3$)-(NNHPh)(PMe$_2$P)$_2$]Br,[47] where the aromatic protons also masked

the β-N$-$H signals. However, the structural parameters associated with the {ReNN(H)C$_5$H$_4$N} moiety of **2** are consistent with those previously observed for isodiazene structures of the general type {MNNR$_2$},[49] and the final difference maps in the X-ray crystallography unambiguously exhibit electron density associated with the β-N$-$H site. The ^{31}P NMR spectrum shows a signal at δ 8.7 ppm.

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Table 4. Atomic Positional Parameters ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{Å}^2 \times 10^3$) for [Re{2-(Ph$_2$P)C$_6$H$_4$S}$_2$(NNC$_5$H$_4$N)] (**5**)

	x	y	z	U(eq)
Re(1)	1690(1)	6792(1)	1379(1)	18(1)
P(1)	799(1)	7528(1)	443(1)	19(1)
P(2)	2761(1)	6003(1)	2242(1)	21(1)
S(1)	3198(1)	7764(1)	1599(1)	23(1)
S(2)	2792(1)	6030(1)	627(1)	25(1)
N(1)	269(4)	7059(2)	1868(2)	21(1)
N(2)	−852(4)	6793(2)	1983(2)	28(1)
N(3)	52(4)	5936(2)	1270(2)	24(1)
C(1)	−995(5)	6119(3)	163(2)	26(1)
C(2)	−2130(5)	5668(3)	1658(3)	39(1)
C(3)	−2202(6)	5021(3)	1305(3)	47(1)
C(4)	−1141(6)	4827(3)	928(3)	40(1)
C(5)	−47(6)	5292(3)	922(2)	31(1)
C(6)	1682(5)	8409(2)	502(2)	23(1)
C(7)	1400(6)	8977(3)	31(2)	32(1)
C(8)	2189(6)	9603(3)	43(3)	40(1)
C(9)	3281(6)	9661(3)	524(3)	43(1)
C(10)	3568(6)	9109(3)	1003(3)	33(1)
C(11)	2765(5)	8472(2)	992(2)	23(1)
C(12)	979(5)	7282(2)	−443(2)	21(1)
C(13)	2282(5)	7242(3)	−644(2)	27(1)
C(14)	2490(5)	7094(3)	−1316(2)	29(1)
C(15)	1417(6)	6975(3)	−1788(2)	33(1)
C(16)	122(6)	7010(3)	−1599(2)	34(1)
C(17)	−102(5)	7164(3)	−925(2)	28(1)
C(18)	−997(4)	7697(3)	485(2)	24(1)
C(19)	−1890(5)	7112(3)	384(2)	29(1)
C(20)	−3235(6)	7188(3)	495(3)	37(1)
C(21)	−3685(6)	7860(4)	710(3)	45(1)
C(22)	−2808(6)	8452(4)	811(3)	45(1)
C(23)	−1469(5)	8375(3)	695(3)	33(1)
C(24)	3569(5)	5251(3)	1810(2)	28(1)
C(25)	4180(6)	4656(3)	2164(3)	38(1)
C(26)	4625(6)	4055(3)	1823(3)	44(1)
C(27)	4496(6)	4056(3)	1112(3)	43(1)
C(28)	3944(5)	4655(3)	753(3)	36(1)
C(29)	3473(5)	5270(3)	1104(2)	29(1)
C(30)	4077(5)	6313(3)	2883(2)	25(1)
C(31)	4003(5)	6207(3)	3576(2)	31(1)
C(32)	5045(5)	6458(3)	4036(3)	35(1)
C(33)	6148(6)	6801(3)	3809(3)	41(1)
C(34)	6234(6)	6908(3)	3117(3)	44(1)
C(35)	5189(5)	6666(3)	2655(3)	34(1)
C(36)	1499(5)	5552(3)	2714(2)	27(1)
C(37)	1143(6)	4809(3)	2621(3)	35(1)
C(38)	65(7)	4521(4)	2926(3)	50(2)
C(39)	−663(6)	4959(4)	3325(3)	46(2)
C(40)	−347(6)	5691(4)	3418(3)	39(1)
C(41)	751(5)	5988(3)	3118(2)	28(1)

A similar protocol was used to isolate [ReCl$_3$(PPh$_3$)$_2$-(NNC$_3$H$_4$N$_2$)] (**3**), starting from 2-hydrazino-2-imidazoline. In this case, a one-step synthesis was employed starting from NH$_4$ReO$_4$. The reaction mixture contained NH$_4$ReO$_4$, PPh$_3$, and 2-hydrazino-2-imidazoline in an acidic ethanol solution. After refluxing, a blue-green solid precipitated in good yield. The IR spectrum displays a medium intensity band at 1533 cm^{-1} assignable to ν(N=N) of the organodiazene, along with two strong bands between 700 and 750 cm^{-1} attributable to the presence of triphenylphosphine. The assumption in this case is that the rhenium oxidation state is again +3 with the organodiazene ligand acting as a neutral ligand, but the conclusion is based solely on analogy to other members of the series and not on definitive evidence. Attempts to grow crystals of **3** for X-ray studies were unsuccessful.

The reactions of **1** with phosphinoarenethiols (abbreviated P−(SH)x; x = 1, 2), chelating ligands with thiolate sulfur and tertiary phosphorus atoms as donors, have been also studied.

The results show that, in order to maintain the coordination number and the oxidation state of the metal, the substitution of the incoming ligand for the chlorine atoms can be accompanied by deprotonation of the organodiazene ligands.

Reaction of [ReCl$_3$(NNC$_5$H$_4$NH)(HNNC$_5$H$_4$N)] (**1**) with 2-(Ph$_2$P)C$_6$H$_4$SH and Et$_3$N in methanol gives [Re{η^2-2-(Ph$_2$P)-C$_6$H$_4$S}{η^1-2-(Ph$_2$PO)C$_6$H$_4$S}(η^1-NNC$_5$H$_4$N)(η^2-HNN-C$_5$H$_4$N)] (**4**). In this reaction, the three chlorine atoms of the precursor have been replaced by a (P,S) bidentate phosphino thiolate ligand and by a monodentate phosphinyl thiolate ligand coordinated to the metal through the thiolate sulfur atom. X-ray studies confirm the presence of ligands of both types (vide infra). The oxygen atom of the phosphinyl thiolate moiety most likely originates from oxygen dissolved in the solvent, since rigorously degassed solutions do not yield isolable products. The metal is further coordinated to a η^2-(N,N) neutral organodiazene ligand and to an anionic η^1-pyridyldiazenido ligand. In this way, the metal is in an octahedral [ReN$_3$PS$_2$] environment. The IR spectrum of the compound shows absorptions characteristic of the organodiazene ligand and also bands in the aromatic region belonging to the phosphino thiolate ligand. The spectrum also shows a medium-intensity band at 1120 cm^{-1} attributed to ν-(P−O). The compound exhibits diamagnetic behavior, and the ^{1}H NMR spectrum shows a multiplet at δ 8.8−6.3 ppm characteristic of the aromatic protons and a singlet at δ 12.0 ppm due to the α-N−H proton of the η^2-pyridyldiazene. The ^{31}P NMR spectrum shows two signals at δ 29.1 and 28.3 ppm for the inequivalent phosphorus atoms.

The same reaction produces [Re{2-(Ph$_2$P)C$_6$H$_4$S}$_2$(NNC$_5$H$_4$N)] (**5**), isolated from the filtrate of **4**. In **5**, the rhenium atom is coordinated by two chelating phosphino thiolate ligands and by an anionic η^2-(N,N) pyridyldiazenido ligand. Consequently, the three chlorine atoms and the η^1-pyridiniumyldiazenido ligand have been replaced by two phosphino thiolate ligands. To maintain the oxidation state of the rhenium atom, the neutral pyridyldiazene ligand of the precursor is deprotonated so as to be formally a η^2-organodiazenido group. The IR spectrum of this complex is similar to that of **4**, but the band attributed to ν(P−O) is absent. The FAB mass spectrum shows the molecular peak at m/z 880 and also a fragment of m/z at 773, which corresponds to the ion [Re{2-(Ph$_2$P)C$_6$H$_4$S}$_2$]$^+$. The ^{1}H NMR spectrum shows multiplets between δ 8.0 and 6.4 ppm due to the aromatic hydrogen atoms and a doublet at δ 8.2 ppm assignable to the α-proton of the pyridine ring. The ^{31}P NMR spectrum exhibits a quadruplet characteristic of an AB system, showing that in solution the two phosphorus atoms are non-equivalent. The phosphorus sites are not interconvertible up to 60 °C, the temperature limit in acetonitrile.

To evaluate possible steric effects on the structural chemistry of the rhenium−phosphino thiolate system, the precursor [ReCl$_3$-(HNNC$_5$H$_4$N)(NNC$_5$H$_4$NH)] (**1**) was treated with a solution of 2-(diphenylphosphinyl)-6-(trimethylsilyl)benzenethiol in methanol in the presence of triethylamine. The solid obtained was identified as [ReCl{2-(Ph$_2$PO)-6-(Me$_3$Si)C$_6$H$_3$S}(NNC$_5$H$_4$N)-(HNNC$_5$H$_4$N)] (**6**). This compound is the result of the substitution of two chlorine atoms of **1** by an anionic bidentate phosphinyl thiolate ligand and the simultaneous deprotonation of the pyridiniumyldiazenido ligand. While the reaction of **1** with 2-(diphenylphosphinyl)benzenethiol produces **2**, with the substitution of all the chlorine atoms, in the case of 2-(diphenylphosphinyl)-6-(trimethylsilyl)benzenethiol, the steric bulk of the ligand apparently precludes the ligation of a second phosphinyl thiolate ligand in the presence of the pyridyldiazenido ligand. The FAB mass spectrum of **6** shows a peak at
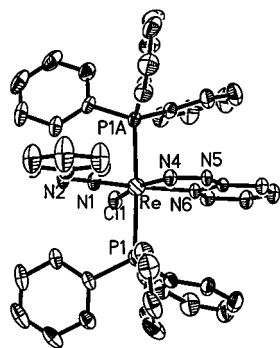
Figure 1. View of the molecular cation of [ReCl(PPh₃)₂(NHNC₅H₄N)-(HNNC₅H₄N)]Cl₂ (**2**), showing the atom-labeling scheme and 50% thermal ellipsoids.
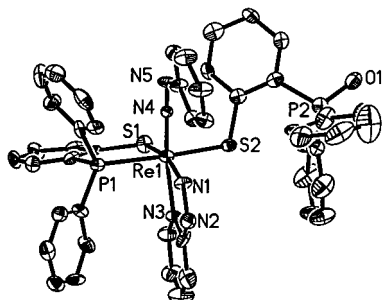
Figure 2. ORTEP representation of the structure of [Re{2-(Ph₂P)-C₆H₄S}]{2-(Ph₂PO)C₆H₄S}(NNC₅H₄N)(HNNC₅H₄N)] (**4**), showing the atom-labeling scheme and 50% thermal ellipsoids.

m/z 814, which corresponds to [ReCl{2-(Ph₂PO)-6-(Me₃Si)-C₆H₃S}(NNC₅H₄N)(HNNC₅H₄N)]⁺, and also a fragment at *m/z* 779, corresponding to [Re{2-(Ph₂PO)-6-(Me₃Si)C₆H₃S}-(NNC₅H₄N)(HNNC₅H₄N)]. The ¹H NMR spectrum of **6** shows the anticipated aromatic signals, the singlet of the NH group at δ 12.0 ppm, and a signal at δ 0.3 ppm assigned to the methyl protons of the trimethylsilyl group.

The chemistry of the related tridentate ligand PhP(C₆H₄SH-2)₂ was also investigated to evaluate the influence of ligand denticity on the reaction chemistry and product identity. The reaction of this ligand with **1** in methanol in the presence of Et₃N gives [Re{PhP(C₆H₄S-2)₂}(NNC₅H₄N)(HNNC₅H₄N)] (**7**). Attempts to obtain crystals suitable for X-ray studies were unsuccessful. The analytical data are in agreement with this formulation, and the FAB mass spectrum shows peaks at *m/z* 723, assigned to [Re{PhP(C₆H₄S-2)₂}(NNC₅H₄N)(HNNC₅H₄N)]⁺, and at *m/z* 616, corresponding to [Re{PhP(C₆H₄S-2)₂}-(NNC₅H₄N)]⁺. The absence of the ν(S—H) in the IR spectrum and the absence of the signal for the ⁻SH proton in the ¹H NMR spectrum show that both thiol groups are deprotonated in the complex. The ¹H NMR spectrum also shows a signal at δ 15.4 ppm characteristic of a hydrogen atom bound to the α-nitrogen of a neutral η²-pyridyldiazene ligand. The ³¹P NMR spectrum exhibits a signal at δ 38.2 ppm. The ³¹P NMR spectrum of free PhP(C₆H₄SH-2)₂ shows a signal at δ −21.3 ppm, and the shift to lower field on going from the free ligand to the complex can be taken as a demonstration of coordination of the phosphorus atom to the metal.

Description of Structures. The molecular structures of **2**, **4**, and **5**, together with the atomic numbering schemes adopted, are shown in Figures 1−3. Selected bond distances and angles are given in Tables 5−7.

In [ReCl(PPh₃)₂(η¹-NHNC₅H₄N)(η²-HNNC₅H₄N)]Cl₂ (**2**), the rhenium atom lies at the center of a distorted octahedron as illustrated in Figure 1. The metal is surrounded by two trans
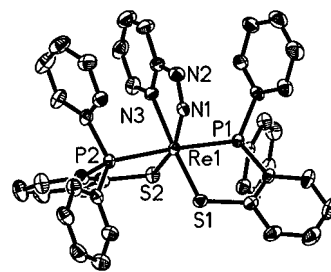

Figure 3. View of the structure of [Re{2-(Ph₂P)C₆H₄S}₂(NNC₅H₄N)] (**5**), showing the atom-labeling scheme and 50% thermal ellipsoids.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for [ReCl(PPh₃)₂(NHNC₅H₄N)(HNNC₅H₄N)]Cl₂ (**2**)

Re(1)−N(1)	1.777(7)	Re(1)−N(4)	1.902(7)
Re(1)−N(6)	2.191(7)	Re(1)−Cl(1)	2.390(2)
Re(1)−P(1)	2.502(2)	Re(1)−P(1)	2.502(2)
N(2)−C(1)	1.385(13)	N(1)N(2)	1.263(10)
N(3)−C(1)	1.44(2)	N(3)−C(5)	1.37(2)
N(5)−C(6)	1.353(11)	N(4)−N(5)	1.267(10)
N(1)−Re(1)−N(4)	93.5(3)	N(1)−Re(1)−N(6)	168.0(3)
N(4)−Re(1)−N(6)	74.5(3)	N(1)−Re(1)−Cl(1)	106.6(3)
N(4)−Re(1)−Cl(1)	159.9(2)	N(6)−Re(1)−Cl(1)	85.4(2)
N(1)−Re(1)−P(1)	92.83(5)	N(4)−Re(1)−P(1)	96.14(4)
N(6)−Re(1)−P(1)	88.55(5)	Cl(1)−Re(1)−P(1)	83.13(4)
P(1)−Re(1)−P(1)	166.14(7)	Re(1)−N(1)−N(3)	175.9(7)
Re(1)−N(4)−N(5)	123.7(6)		

Table 6. Selected Bond Lengths (Å) and Angles (deg) for [Re{2-(Ph₂P)C₆H₄S}{2-(PH₂PO)C₆H₄S}(NNC₅H₄N)(HNNC₅H₄N)] (**4**)

Re(1)−N(4)	1.779(14)	Re(1)−N(1)	1.93(2)
Re(1)−N(3)	2.17(2)	Re(1)−S(1)	2.398(5)
Re(1)−P(1)	2.436(5)	Re(1)−S(2)	2.452(5)
N(1)−N(2)	1.34(2)	P(2)−O(1)	1.49(2)
N(4)−Re(1)−N(1)	91.5(7)	N(4)−Re(1)−N(3)	162.3(6)
N(1)−Re(1)−N(3)	71.0(7)	N(4)−Re(1)−S(1)	107.5(5)
N(1)−Re(1)−S(1)	160.9(5)	N(3)−Re(1)−S(1)	90.1(5)
N(4)−Re(1)−P(1)	90.6(5)	N(1)−Re(1)−P(1)	95.0(5)
N(3)−Re(1)−P(1)	92.9(4)	S(1)−Re(1)−P(1)	83.1(2)
N(4)−Re(1)−S(2)	94.6(5)	N(1)−Re(1)−S(2)	99.0(5)
N(3)−Re(1)−S(2)	86.5(4)	S(1)−Re(1)−S(2)	81.9(2)
P(1)−Re(1)−S(2)	164.9(2)	Re(1)−N(1)−N(2)	128.9(13)
Re(1)−N(4)−N(5)	174(2)		

Table 7. Selected Bond Lengths (Å) and Angles (deg) for [Re{2-(Ph₂P)C₆H₄S}₂(NNC₅H₄N)] (**5**)

Re(1)−N(1)	1.855(4)	Re(1)−N(3)	2.257(4)
Re(1)−S(1)	2.3405(11)	Re(1)−S(2)	2.3768(11)
Re(1)−P(1)	2.3990(11)	Re(1)−P(2)	2.4125(11)
N(1)−N(2)	1.260(5)		
N(1)−Re(1)−N(3)	69.4(2)	N(1)−Re(1)−S(1)	102.40(12)
N(3)−Re(1)−S(1)	171.78(10)	N(1)−Re(1)−S(2)	154.17(12)
N(3)−Re(1)−S(2)	84.85(10)	S(1)−Re(1)−S(2)	103.37(4)
N(1)−Re(1)−P(1)	90.56(11)	N(3)−Re(1)−P(1)	95.33(10)
S(1)−Re(1)−P(1)	84.99(4)	S(2)−Re(1)−P(1)	89.99(4)
N(1)−Re(1)−P(2)	95.56(11)	N(3)−Re(1)−P(2)	86.08(10)
S(1)−Re(1)−P(2)	94.48(4)	S(2)−Re(1)−P(2)	84.14(4)
P(1)−Re(1)−P(2)	173.83(4)	Re(1)−N(1)−N(2)	136.8(3)

triphenylphosphines, two organodiazenes, and a chlorine atom. The rhenium complex cation is charge-balanced by two co-crystallized chlorine atoms. The two organodiazene ligands adopt distinct binding modes, one coordinating through both the α-nitrogen and the pyridyl nitrogen and the other coordinating monodentately through the α-nitrogen. The protonation pattern of the bidentate organodiazenes is consistent with other examples reported in recent years. The monodentate organodiazene, while having the geometrical pattern of being depro-

Table 8. Comparison of Bond Lengths and Angles for Organodiazene and Organodiazenido Ligands in Rhenium Complexes

complex	Re−N, Å	N−N, Å	M−N−N, deg	N−N−C, deg
[ReCl₃(η²-HNNC₅H₄N)(η¹-NNC₅H₄NH)][39]	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)
[ReCl₂(PPh₃)(η²-HNNC₅H₄N)(η¹-NNC₅H₄N)][48]	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)
[ReCl₂(PPh₂)₂(η²-NNC₅H₄N)][49]	1.815(8)	1.256(12)	137.3(7)	105.8(8)
	2.174(8)			
[ReCl₂(PPh₃)(η²-HNNC₅H₄N)(η¹-NHNC₅H₄N)]Cl₂ (**2**)	1.902(7)	1.271(10)	123.1(6)	119.8(7)
	2.191(7)			
	1.776(7)	1.265(9)	175.9(7)	115.8(8)
[Re{η²-2-(Ph₂P)C₆H₄S}{η¹-2-(Ph₂PO)C₆H₄S}-(η²-HNNC₆H₄N)(η¹-NNC₅H₄N)] (**4**)	1.93(2)	1.34(2)	128.9(13)	108(2)
	2.17(2)			
	1.779(14)	1.25(2)	174(2)	119(2)
[Re{η²-2-(Ph₂P)C₆H₄S}₂(η²-NNC₅H₄N)] (**5**)	1.855(4)	1.260(5)	136.8(3)	107(3)

tonated throughout, does not exhibit the extensive multiple-bond character of such a diazenido(1−) species described in previous reports[45] and in this work; therefore the ligand must be another neutral diazene. The position of the proton was tentatively located on the β-nitrogen. The pyridyl nitrogen is inaccessible due to the steric influence of the bidentate diazene ring, while the α-nitrogen geometry, with Re−N(1) and N(1)−N(2) of 1.777(7) and 1.263(10) Å, respectively, is not consistent with protonation at this site. In this complex, the chelate ligand, the chlorine atom, and the pyridyldiazenido ligand are effectively coplanar with the chlorine atom trans to the organodiazene α-nitrogen. The bulky triphenylphosphine ligands occupy axial coordination sites in a trans orientation. The principal distortion from the ideal geometry is the small bite angle of the organodiazene chelate, N(4)−Re−N(6) of 74.5(3)°. The rhenium−chloride bond length of 2.390(2) Å is unexceptional and similar to that found in [ReCl₃(NNC₅H₄N)(HNNC₅H₄N)], with an average value 2.393(3) Å.[39] The average Re−P bond distance of 2.502 Å is larger than that found in [ReCl₂(PPh₃)(NNC₅H₄N)-(HNNC₅H₄N)],[41] showing the influence of two mutually trans phosphorus atoms. The Re−N(6) bond distance of 2.191(7) Å is characteristic of a single bond. The rhenium−nitrogen bond distance to the α-nitrogen atom of the organodiazene chelate, Re−N(4) at 1.902(7) Å, is shorter than a rhenium single bond but longer than that observed in **5** of 1.855(4) Å, reflecting the difference between neutral and anionic forms of this ligand. The other bond distances within the five-member chelate ring show delocalization throughout the organodiazene ligand. The monodentate pyridyldiazenido bond lengths for Re(1)−N(1) and the bond distance for N(1)−N(2) confirm the notion of multiple-bond character throughout the diazenide unit.

The structure of [Re{η²-2-(Ph₂P)C₆H₄S}{η¹-2-(Ph₂PO)-C₆H₄S}(η¹-NNC₅H₄N)(η²-HNNC₅H₄N)] (**4**) shows that the phosphino thiolate is bidentate (P,S) while the phosphinyl thiolate is monodentate (S). The metal is in an {ReN₃S₂P} octahedral environment through coordination to the sulfur atom of the monodentate phosphinyl thiolate ligand, to the sulfur and a phosphorus atoms of the bidentate phosphino thiolate ligand, to a neutral bidentate η²-pyridyldiazene ligand, and finally to a η¹-pyridyldiazenido ligand. The distorted octahedral geometry has the three nitrogen atoms and the sulfur atom S(1) in the equatorial plane and P(1) and S(2) occupying the axial positions with a P(1)−Re−S(2) angle of 164.9(2)°. This observation and the acute angles associated with the N(1)−Re−N(3) and S(1)−Re−P(1) chelates are the principal sources of distortion from a regular octahedral geometry. The Re−N(1), Re−N(3), and Re−N(4) bond distances of 1.93(2), 2.17(2), and 1.779(14) Å, respectively, are in the range of those observed in **2**. The arrangement Re−N(4)−N(5) in the η¹-diazenido ligand is nearly

linear with a bond angle 172(2)°, while the bond angle N(4)−N(5)−C(6) is 119(2)°, reflecting sp² hybridization at the β-nitrogen atom. This value is similar to those found in other examples of η¹-organodiazenido−rhenium complexes (Table 8). The Re−S bond distances, 2.398(5) and 2.452(5) Å, are significantly different. The longer Re−S bond corresponds to the sulfur atom trans to the phosphorus atom, suggesting a structural trans influence. These distances and the Re−P distance of 2.436(5) Å are similar to those found in other octahedral Re(III) containing phosphino thiolate ligands (Table 8).

The structure of [Re{η²-2-(Ph₂P)C₆H₄S}₂(η²-NNC₅H₄N)] (**5**) consists of discrete mononuclear species in which a rhenium atom is bonded to two sulfur atoms and two phosphorus atoms of two anionic bidentate phosphino thiolate ligands and also to two nitrogen atoms of a η²-bidentate pyridyldiazenido ligand, to give a {ReN₂P₂S₂} distorted octahedral geometry. The phosphorus atoms are disposed in a trans fashion, with the P(1)−Re−P(2) angle at 173.83(4)°. The main source of distortion from regular octahedral geometry is again the narrow bite angle of the bidentate diazenide ligand, 69.4(2)°. The Re−N(3) bond distance to the pyridine nitrogen of 2.257(4) Å is slightly longer than those observed in **2** and **4**, suggesting the absence of multiple-bond character. The Re−N(1) distance to the diazenide α-nitrogen, 1.855(4) Å, is intermediate between a single and a double bond. This observation and the value of 1.260(5) Å found for the N−N bond distance are indicative of delocalization and multiple bonding throughout the chelating ring. These values are similar to those found in [ReCl₂(Ph₃P)₂(NNC₅H₄N)],[45] where the organodiazenido ligand is coordinated in an analogous fashion. The two Re−P bond distances of 2.3390(11) and 2.4125(11) Å and the Re−S bond distances of 2.3405(11) and 2.3768(11) Å are unexceptional.

Conclusions

The facile reduction of perrhenate by PPh₃ and hydrazino-pyridine in acidic water/methanol yields the unusual cationic Re(III)−hydrazido species [ReCl(PPh₃)₂(NHNC₅H₄N)(HNN-C₅H₄N)]²⁺ as the chloride salt. The structure of **2** reveals the persistence of the {Re(η²-HNNC₅H₄N)(η¹-NN(H)C₅H₄N)} core in a variety of ligand environments. With varying protonation patterns, this robust core has been observed in the materials with {RePSS′N₃} (**4**), {ReClSON₃} (**6**), and {RePS₂N₃} (**7**) coordination geometries. However, it is also apparent that, under forcing conditions, the monodentate organohydrazino ligand may be displaced, as in the case of [Re{2-(Ph₂P)C₆H₄S}₂-(NNC₅H₄N)] (**5**).

Detailed synthetic and structural studies of complexes with the Re− and Tc−organohydrazino cores have revealed a

complex coordination chemistry, manifested in both monodentate terminal and bidentate linkages and by several distinct patterns for the relative orientations of the ligands within the $\{M(\eta^1\text{-NNR})(\eta^2\text{-HNNR})\}$ cores, which reflect both the metal electronic requirements and the degree of ligand protonation. It is not surprising that many ^{99m}Tc−HYNIC−BAM (biologically active molecule) complexes are mixtures of materials as demonstrated by radio-HPLC.[38b] While the chemistry of the pyridylhydrazino ligand demonstrates the facility of complex formation and the robust nature of such materials, it also suggests a variety of coordination modes for the radiopharmaceutical materials. Since the formulation and mechanistic studies of metal−HYNIC−BAM radiochemical species require homogeneous materials with favorable pharmacokinetics, the synthesis of high-purity compositions continues to demand attention. Our further elaboration of the coligand theme will be presented in a number of forthcoming publications which establish that a variety of thiolate coligands provide homogeneous radiophar-

maceutical preparations with improved stability, rapid localization and retention at the site of infection, constant or decreased concentrations in normal tissues, and no adverse biological effects.[50]

Supporting Information Available: Listings of crystal data, atomic coordinates, bond lengths and angles, anisotropic temperature factors, and calculated hydrogen atom positions and isotropic thermal parameters for the structures of **2**, **4**, and **5**. This material is available on the Internet free of charge at http://pubs.acs.org.

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