MONOMERIC FIVE-COORDINATE RHENIUM DIAZENIDO AND HYDRAZIDO COMPLEXES WITH AROMATIC THIOLATE LIGANDS: X-RAY STRUCTURES OF [Re(NNC₆H₄-4-Br)₂(SC₆H₃-2,5-Me₂)(PPh₃)₂] AND [ReO(NNMePh)(SPh)₃], AND OF THE SYNTHETIC PRECURSOR [Re(NNC₆H₄-4-Br)₂Cl(PPh₃)₂]

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Abstract—Reaction of $[ReOCl_3(PPh_3)_2]$ with bromophenylhydrazine in methanol yields $[\text{ReCl}(N_2C_6H_4Br)_2(\text{PPh}_3)_2]$ (1). Complex 1 reacts with arylthiolates to give mixtures of $[\text{Re}(\text{SAr})(N_2C_6H_4\text{Br})_2(\text{PPh}_3)_2]$ (2) and $[\text{Re}_2(\text{SAr})_7(\text{NNR})_2]^-$. Complexes 1 and 2 display trigonal bipyramidal geometries with the phosphine ligands occupying the axial sites. A significant feature of the structures is the nonequivalence of the rhenium-diazenido moieties, such that for 1 the Re-N(1) and N(1)-N(2) distances are 1.80(2) and 1.24(3) Å, while Re-N(3) and N(3)-N(4) are 1.73(2) and 1.32(3) Å, and for 2 the Re-N distances are 1.73(1) and 1.80(2) with corresponding N-N distances of 1.32(2) and 1.25(2) Å. Reaction of (PPh_4) [ReO(SPh)₄] (3) with unsymmetrically disubstituted hydrazines affords complexes of the type $[ReO(SPh)_{3}(NMRR')]$ (R = Me, R' = Ph for 4). Complexes 3 and 4 display distorted square pyramidal geometries with the oxo groups apical. The significant feature of the structure of 4 is the nonlinear Re-N(1)-N(2) linkage, exhibiting an angle of 145.6(10)°. The angle does not appear to correlate with a significant contribution from a valence form with sp^2 hybridization at the α -nitrogen. Crystal data: 1: monoclinic space group, $P2_1/n$, a = 12.216(2) Å, b = 19.098(2) Å, c = 20.257(4) Å, $\beta = 106.20(1)^\circ$, V = 4538.3(8) Å³ to give Z = 4; structure solution and refinement based on 1905 reflections converged at R = 0.070. 2: monoclinic space group $P2_1/n$, a = 14.393(2) Å, b = 18.842(3)Å, c = 20.717(4)Å, $\beta = 110.26(1)^{\circ}$, V = 5270.5(8)Å³ to give Z = 4 for D = 1.53 g cm⁻¹; structure solution and refinement based on 4249 reflections to give R = 0.070.3: monoclinic space group $P2_1/n$, a = 12.531(2) Å, b = 24.577(4) Å, c = 16.922(3) Å, $\beta = 99.06(1)^\circ$, V = 5146.2(9) Å³, D = 1.36 g cm⁻³ for Z = 4, 2912 reflections, R = 0.050. 4: monoclinic space group $p2_1/n$, a = 16.137(2) Å, b = 9.863(2) Å, c = 16.668(2) Å, $\beta = 111.12(1)^\circ$, $V = 2474.7(6) \text{ Å}^3$, $D = 1.74 \text{ g cm}^{-3}$ for Z = 4, 2940 reflections, R = 0.066.

Although there have been extensive recent studies of transition-metal complexes with sulfur ligands,¹ relatively few simple monomeric rhenium thiolato complexes have been reported.²⁻⁴ In particular, examples of rhenium thiolato species incorporating small organic molecules are rare. As part of our studies of the binding of small molecules to metal sulfur sites, we have prepared a number of diazeonido- and hydrazido(2-)-rhenium complexes with aromatic thiolato coligands. The organodiazenido group $(NNR)^+$ is formally isoelectronic with the nitrosyl ligand NO⁺ and chemically related to the diazenide unit, —NNH, a potential intermediate in the reduction of dinitrogen to ammonia. Structural studies have confirmed that the organodiazenido ligand may adopt a variety of geometries: "singly bent",⁵ "doubly bent"⁶ and bridging.⁷

Unsymmetrically disubstituted organohydrazines may function as hydrazido(2-) ligands, ---NNRR', which arise formally and often in practice, from the protonation of the terminal nitrogen of the organodiazenido ligand. Once again linear⁸

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and bent⁹ M-N-N frameworks have been observed.

In this paper we report the synthesis and struccharacterization of the five-coordinate tural mononuclear rhenium diazenido and hydrazido(2-) complexes [Re(NNC₆H₄Br-4)₂(SC₆H₃- $2,5-Me_2)(PPh_3)_2$ and [ReO(NNMe-(2) Ph) $(SC_6H_5)_3$ (4), respectively. Complex 2 was prepared by the reaction of [ReCl(NNC₆H₄Br- $4_2(PPh_3)_2$ (1) with 2,5-dimethylthiophenol. Although the five-coordinate species 1 had been isolated previously,¹⁰ some ambiguity existed with respect to the structural identity, whether mononuclear or chloro-bridged binuclear. This study establishes the mononuclear trigonal bipyramidal structure, analogous to that of $[MoCl(NNMe_2)_2]$ $(PPh_3)_2]^+$.¹¹

The oxo-hydrazido(2-) species (4) was isolated from the reaction of $[ReO(SPh)_4]^-$ (3) with the disubstituted hydrazine by replacement of a thiophenolate group. Although the retention of the oxo group was unanticipated, a similar reaction trend has been observed for $[MoO(SPh)_4]^-$ with disubstituted hydrazines.

DISCUSSION

The most frequently employed synthetic routes to aryldiazenido complexes employ oxidative addition of a diazonium salt or insertion into a metal-hydrogen bond to give a diazene complex which is subsequently deprotonated.¹² The silvlated diazene Me₃SiN₂Ph has also been shown to provide an efficient method of introducing the aryldiazenido function.¹³ Finally, direct reaction of a metal oxo species with an arylhydrazine may proceed by a condensation mechanism, followed by deprotonation, to yield a metal-aryldiazenido complex.¹⁴ Employing the latter methodology, the rhenium(V)-oxo complex [ReOCl₃(PPh₃)₂] reacts with excess p-bromophenylhydrazine in methanol to give 1 as a red-orange precipitate in 70-80% yield The complex exhibits a strong IR band at 1520 cm^{-1} assigned to v(N=N). The X-ray diffraction studies discussed below have established the identity of this species as a mononuclear complex, analogous to the manganese complex $[MnX(N_2Ph)_2(PPh_3)_2]$.¹⁵

Suspension of 1 in warm benzene or methylene chloride gives a red-maroon material with strong IR bands at 1560 and 1520 cm⁻¹. We suspect the occurrence of a dimerization reaction in aprotic solvents giving a doubly chloro-bridged species (1a), implying both linear and bent diazene ligands functioning as three- and one-electron donors.

Complex 1 reacts with excess HCl in methanol to give a red-orange material analyzing for $[\text{ReCl}_2(\text{NNHC}_6\text{H}_4\text{Br}-4)(\text{NNC}_6\text{H}_4\text{Br}-4)(\text{PPh}_3)_2]$ (1b). The complex shows strong IR bands at 1625 and 1572 cm⁻¹ assigned to $\nu(\text{N}-\text{N})$ for the hydrazido(2-)- and diazenido-type ligands. Complex 1b appears to be structurally analogous to the previously reported $[\text{ReBr}_2(\text{N}_2\text{Ph})(\text{NNHPh})(\text{PPh}_3)_2]$ where protonation occurs at the β -nitrogen of the nitrogen ligand.¹⁰

Addition of an excess of 2,5-dimethylthiophenol to 1 results in a dark red solution from which orange crystals of 2 are observed to form in several hours. The characteristic IR bands at 1545 and 1515 cm⁻¹ confirm the presence of the bisorganodiazenidorhenium unit. In the reaction with unsubstituted phenylthiolate, a second crop of lustrous black crystals separates from the mother liquor after several days. This species has been identified as the formally rhenium(II) complex $[\text{Re}_2(\text{SAr})_7(\text{NNC}_6\text{H}_4\text{Br}-4)_2]^-$, isolated as the triethylammonium salt. The structural and chemical properties of this class of complexes have been discussed previously.¹⁶ Although displacement of the chloro ligand of 1 by thiophenolate occurs readily, under the reaction conditions employed substitution of the phosphine ligands and one organodiazenido group by thiolate ligands occurs only slowly to yield the stable triply thiolato-bridged species $[Re_2(SAr)_7(NNR)_2]^{-1}$.

In contrast to the behavior of 1, complex 2 reacts with HCl to produce intractable materials, presumably as a result of protonation at the coordinated thiolate sulfur rather than at nitrogen. This preferential protonation at the thiolate site appears to be characteristic of diazenido-thiolate complexes.

Although there are now several examples of molybdenum hydrazido(2–) complexes with thiolate coligands,¹⁷ analogous rhenium complexes have not been reported. In an attempt to isolate rhenium species of this type, [ReOCl₃(PPh₃)₂] was treated with an excess of an unsymmetrically disubstituted organohydrazine, such as H₂NNMePh, to yield a crystallizine, light orange material analyzing for [ReCl(NNMePh)₂(PPh₃)₂]. Both —NNR₂ ligands cannot serve as four-electron donors, since the metal would have a 20-electron count, suggesting that one —NNR₂ group is bent at the α -nitrogen and functions as a two-electron donor.

Reaction of $[\text{ReCl}(\text{NNMePh})_2(\text{PPh}_3)_2]$ with excess thiophenol in benzene yields 4 in low yield as a diamagnetic bright red crystalline material. The presence of the oxo group is confirmed by a strong IR band at 945 cm⁻¹, while the band at 1545 cm⁻¹ is attributed to the hydrazido(2-) ligand. The oxo ligand is apparently introduced from residual oxygen in the reaction solvent, and yields may be considerably improved by carrying out the synthesis in

1		2		3		4	
Re-Cl(1)	2.436(9)	Be-S (1)	2 376(4)	$\frac{\text{Re-O(1)}}{\text{Re-S(1)}}$	1.661(11)	$\frac{\text{Re-O(1)}}{\text{Re-S(1)}}$	1.658(12)
ReP(1)	2.449(8)	Re - P(1)	2.457(4)	$\frac{Re-S(1)}{Re-S(2)}$	2.320(4)	$\frac{1}{Re-S(2)}$	2.354(4)
Re—P(2)	2.457(9)	Re — P (2)	2.454(4)	$\frac{\text{Re}-S(3)}{\text{Re}-S(4)}$	2.323(5) 2.333(4)	ReS(3)	2.331(4)
ReN(1)	1.798(19)	Re — N (1)	1.730(13)			Re-N(1)	1.858(9)
N(1) - N(2)	1.241(29)	N(1)-N(2)	1.324(17)			N(1)-N(2)	1.255(15)
Re—N(3)	1.726(24)	Re-N(3)	1.798(16)				
N(3)—N(4)	1.315(36)	N(3)N(4)	1.249(23)				

Table 1. Relevant bond lengths (Å) for structures 1-4

oxygenated solvents. The oxo-hydrazido complex (4) may also be prepared by reaction of $[ReO(SPh)_4]^-$ (3) with H₂NNMePh. Although we anticipated the replacement of the oxo group of 3 by a hydrazido(2-) ligand, 3 reacted with the 1,1disubstituted hydrazine with retention of the oxo group and replacement of a thiophenolate group by the hydrazido(2-) ligand to give 4. This is not a simple methathesis reaction as concomitant oxidation of the metal from Re^V to Re^{VII} occurs. A hydrazido(1-) species such as [Re(NHN-MePh)O(SPh)₃]⁻ may be an intermediate. The formation of a rhenium-nitrogen multiple bond may provide the driving force for oxidative elimination of the hydrogen on the α -nitrogen.

DESCRIPTION OF THE STRUCTURES

Relevant bond lengths and angles are tabulated in Tables 1 and 2, and ORTEP views of the structures are presented in Figs 1–4.

Table 2. Relevant bond angles (°) for structures 1-4

1		2		
Re-N(1)-N(2)	172.0(27)	Re—N(1)—N(2)	160.9(2)	
Re-N(3)-N(4)	164.7(18)	Re-N(3)-N(4)	178.1(2)	
N(1)-Re-N(3)	119.4(12)	N(1)—Re— $N(3)$	120.0(6)	
P(1)—Re— $P(2)$	174.8(2)	P(1)— Re — $P(2)$	177.5(2)	
P(1)—Re— $C(1)$	89.7(3)	P(1)—Re— $S(1)$	84.2(1)	
P(2)—Re— $C(1)$	86.5(3)	P(2)—Re— $S(1)$	97.2(1)	
P(1)—Re—N(1)	93.6(8)	P(1)—Re— $N(1)$	90.0(5)	
P(2)—Re—N(1)	91.3(8)	P(2)—Re—N(1)	91.1(5)	
P(1)—Re—N(3)	87.4(9)	P(1)—Re— $N(3)$	90.3(5)	
P(2)—Re—N(3)	91.7(9)	P(2)—Re— $N(3)$	87.2(5)	
C(1)-Re-N(1)	118.1(10)	S(1)—Re— $N(1)$	121.1(5)	
C(1)-Re-N(3)	122.5(7)	S(1)—Re—N(3)	118.6(4)	
N(1)—N(2)—C(71)	120.0(26)	N(1)—N(2)—C(71)	119.8(13)	
N(3)N(4)C(81)	116.2(23)	N(3)—N(4)—C(81)	117.6(14)	
3		4		
		Re-N(1)-N(2)	145.6(10)	
O(1)—Re— $S(1)$	109.3(4)	O(1)—Re— $S(1)$	109.9(4)	
O(1)—Re— $S(2)$	106.7(4)	O(1)—Re—S(2)	104.8(4)	
O(1)—Re—S(3)	109.2(4)	O(1)—Re— $S(3)$	109.4(4)	
O(1)-Re-S(4)	107.0(4)	O(1)—Re— $N(1)$	108.2(5)	
S(1)—Re—S(2)	84.8(2)	S(1)—Re—S(2)	77.4(1)	
S(1)—Re— $S(3)$	141.5(2)	S(1)—Re— $S(3)$	140.0(2)	
S(1)—Re— $S(4)$	84.8(2)	S(2)—Re— $S(3)$	85.7(1)	
S(2)—Re—S(4)	146.3(2)	S(1)— Re — $N(1)$	88.8(3)	
S(3)—Re—S(4)	83.4(2)	S(2)—Re— $N(1)$	146.9(4)	
		S(3)—Re— $N(1)$	86.1(4)	
		N(1) - N(2) - C(1)	118.8(12)	
	,	N(1) - N(2) - C(7)	122.0(11)	



Fig. 1. ORTEP view of the structure of [ReCl(NNC₆H₄-Br-4)₂(PPh₃)₂], showing the atom-labelling scheme.



Fig. 2. Perspective views of the structure of $[Re(SC_6H_3-2,5-Me_2)(NNC_6H_4-Br-4)_2(PPh_3)_2]$.



Fig. 3. ORTEP view of the structure of [ReO(SPh)₄]⁻, crystallized as the (PPh₄)⁺ salt.

The structure of 1 consists of discrete monomeric units. The geometry about the rhenium is best described as a trigonal bipyramidal, with the phosphine ligands axial and the equatorial plane defined



Fig. 4. ORTEP view of the structure of [ReO(NNMePh) (SPh)₃], showing the atom labelling.

by the chloro group and the α -nitrogen atoms of the diazenido ligands. The rhenium-phosphorus and rhenium-chlorine distances are unexceptional. However, an unusual feature of the structure is the inequivalence of the two rhenium-diazenido units. The Re(1)—N(1) distance of 1.80(1) Å is significantly longer than the Re(1)-N(3) distance [1.73(2) Å]. This unequivalence is reflected in the N(1)-N(2) and N(3)-N(4) distances of 1.24(2) and 1.32(3) Å, respectively, and in the Re-N(1)-N(2) and Re-N(2)-N(3) angles of 172.0(23) and 164.7(18)°. As shown in Table 3, this feature is also observed in the structures of 2 the molybdenum(VI) cationic species and $[MoCl(NNMe_2)_2(PPh_3)_2]^{+16}$ which is structurally analogous to 1 and 2. Since there are no apparent steric interactions between the --- NNR or --- NNR₂ ligands and the phosphine groups, this does not appear to be simply a solid-state effect.

The gross structural features of 2 are essentially identical to those of 1, with the exception of the substitution of the thiophenolate ligand for the chloro group in the equatorial plane. The inequivalence of the diazenido ligands is pronounced, suggesting varying contributions of canonical forms I and II to the overall structure of the diazenido ligands. The Re—N(3) and N(3)—N(4) distances of 1.80(2) and 1.24(2) Å closely approximate the limiting formalism I, for which distances of 1.80 and 1.24 Å have been calculated.¹⁸ On the other

Complex	Coordination geometry ^a	M—N (Å)	N—N (Å)	M—N— N (°)	Reference
$[\text{ReCl}(\text{NNC}_{6}\text{H}_{4}\text{Br-4})_{2}(\text{PPh}_{3})_{2}]$	tbp	1.73(2)	1.32(3)	164.7(18)	This work
	-	1.80(2)	1.24(2)	172.0(23)	
$[\text{Re}(\text{SC}_{6}\text{H}_{3}-2,5-\text{Me}_{2})(\text{NNC}_{6}\text{H}_{4}\text{Br}-4)_{2}(\text{PPh}_{3})_{2}]$	tbp	1.73(1)	1.32(2)	160.9(13)	This work
	-	1.80(1)	1.25(2)	178.1(13)	
$[MoCl(NNMe_2)_2(PPh_3)_2]^+$	tbp	1.76(1)	1.34(2)	165.2(10)	14
	-	1.76(1)	1.25(1)	173.9(9)	
[ReO(NNMePh)(SPh) ₃]	sq. pyr.	1.858(9)	1.26(2)	145.6(10)	This work
[MoO(NNMe ₂)(SPh) ₃] ⁻	sq. pyr.	1.821(9)	1.29(1)	152.5(10)	11

Table 3. Comparison of geometric features of five-coordinate rhenium and molybdenum diazenido and hydrazido(2-) complexes

^a tbp = trigonal bypiramidal, sq. pyr. = square pyramidal.

hand, the Re—N(1) and N(1)—N(2) distances of 1.73(1) and 1.32(2) Å suggest a significant contribution from II and a degree of valence isomerism for the diazenido-rhenium units of these structural types.



The structure of 3, crystallized as the tetraphenylphosphonium salt, is identical to that of the tetraphenylarsonium salt, previously reported.² The geometry about the rhenium is square pyramidal with an apical oxo group. The Re—O distance of 1.66(1) Å is similar to those observed for the (Ph₄As)⁺ salt, and for [ReO(SCH₂CH₂S)₂]⁻⁴ and [ReO(SC₆H₂Me₃)₄]^{-.19}

The geometry about the rhenium in 4 is best described as distorted square pyramidal with the oxo ligand occupying the apical position. The basal plane is defined by three thiolato sulfur atoms and the α -nitrogen of the hydrazido(2-) ligand. The Re atom lies *ca* 0.7 Å above the mean NS₃ basal plane.

The Re—O distance of 1.66(1) Å is identical to that observed for the parent anion (3), and the average Re—S distance of 2.341(6) Å is similar to that of 2.333(6) Å in 3. The Re—S(3) distance is longer than the average of the Re—S(1) and Re—S(2) distances [2.354(4) vs 2.335(4) Å], presumably reflecting a *trans* influence of the hydrazido(2-) ligands in the pseudo-*trans* position.

The overall square pyramidal geometry adopted by **4** is similar to that observed for $[MoO(NNMe_2)$ $(SPh)_3]^{-.11}$ The presence of the oxo group in the apical position is consistent with the tendency of cylindrically symmetrical π -donors to occupy this site in order to maximize overlap with the metal d_{xz} - and d_{yz} -orbitals.²⁰

The Re-N(1) and N(1)-N(2) distances of 1.858(9) and 1.26(2) Å, respectively, lie within the range found for metal hydrazido(2-) complexes,²¹ and are consistent with extensive delocalization of the π -bonding throughout the Re-N(1)-N(2) unit. Although the --- NNMePh ligand lies in the basal plane, the Re-N(1) distance indicates strong π -bonding to the rhenium. The hydrazido group has two orbitals available for π -bonding, the porbital on N(1) in the N(1)-N(2)-C(1)-C(7) plane and the N–N π -antibonding orbital perpendicular to this plane. The N(1)-N(2)-C(1)-C(7) plane eclipses the Re-O bond vector, ensuring that the N(1) p-orbital overlaps with the metal D_{z^2} orbital. The π -antibonding orbital has the correct symmetry to interact with the metal d_{xy} -orbital.

The most unusual feature of the structure is the non-linearity of the Re-N(1)-N(2) angle $[145.6(10)^{\circ}]$. Simple electron counting suggests that -NNR₂ unit functions as a four-electron donor in the hydrazido(2-) formalism. Although the short N(1)—N(2) distance supports this argument, the Re-N(1)-N(2) angle suggests a contribution from a valence form with sp^2 hybridization at the α -nitrogen. This latter description of the bonding appears unlikely in view of the short Re-N(1) distance and the electronic requirements of the metal. Recent ab initio calculations indicate that the energies between different geometric forms of -NNR₂ ligand types may often be very small and that the angle at the α -nitrogen is a rather insensitive indicator of hybridization mode.²² Consequently, extrapolating from the observed structure to an inferred charge distribution may be inappropriate.

Five-coordinate geometries appear to be quite common for rhenium complexes with strongly π -

bonding ligands, such as oxo groups and hydrazido or diazenido units. The limiting geometry, whether trigonal bipyramidal or square-based pyramidal, may be dictated in part by the steric requirements of the coligands. Thus, in the presence of bulky coligands, such as phosphines, the trigonal bipyramidal geometry is adopted with the bulky groups occupying the axial sites. Cylindrically symmetrical π -donors, such as oxo groups, appear to favor the apical position of the square-based pyramid.

Table	Summary of crystal data and experi	mental details for the st	ructures of [ReCl(NNC ₆ H	$[_4Br-4)_2(PPh_3)_2](1),$
	$[Re(SC_6H_3-2,5-Me_2)(NNC_6H_4Br-4)_2(I)]$	PPh_{3}_{2}] (2), (PPh_{4})[ReO(SPh) ₄] (3) and [ReO(NNR	$_{2})(SPh)_{3}](4)$

	1	2	3	4	
anna dh'fhilid di baran an a	(A) Crystal J	parameters at 23°C ^a			
a (Å)	12.216(2)	14.393(3)	12.531(2)	16.137(2)	
$b(\mathbf{A})$	19.098(3)	18.842(3)	24.577(4)	9.863(2)	
$c(\mathbf{A})$	20.257(4)	20.717(4)	16.922(3)	16.668(2)	
α (°)	90.00	90.00	90.00	90.00	
β (°)	106.20(1)	110.26(1)	99.06(1)	111.12(1)	
γ (°)	90.00	90.00	90.00	90.00	
$V(Å^3)$	4538.3(8)	5270.5(8)	5146.2(9)	2474.7(6)	
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$	
Ζ	4	4	4	4	
$D_{\rm calc} ({\rm g}{\rm cm}^{-3})$	1.63	1.53	1.36	1.74	
	(B) Measuren	nent of intensity data	1		
Crystal dimension (mm)	$0.20 \times 0.20 \times 0.25$	$0.15 \times 0.20 \times 0.22$	0.18×0.22×0.15	$0.18 \times 0.18 \times 0.18$	
Instrument	Nicolet R3m				
Radiation	Mo- K_{α} ($\lambda = 0.7106$	59 Å)			
Scan mode	Coupled θ (crystal)	-2θ (counter)			
Scan rate (° min^{-1})	7-30				
Scan range (°)	$2 > 2\theta \leq 45$				
Scan length (°)	From $[2\theta(K_{\alpha_1}) - 1.0]$ to $[2\theta(K_{\alpha_2}) + 1.0]$				
Background measurement	Stationary crystal, stationary counter, at the beginning and end of each 2θ scan,				
Standard	3 collected every 1	97			
Number of reflections collected	4757	8550	5363	4922	
Number of independent reflection	S				
used in solution	1905	4249	2912	2940	
(C) Reduction of	intensity data and su	ummary of structure	solution and refinem	ient ^b	
Data corrected for background	, attenuators, Lorent	z and polarization e	ffects in the usual fas	hion	
Absorption coefficient (cm^{-1})	67.91	58.41	44.24	92.25	
Absorption correction	Based on ψ scands	for five reflections v	vith χ near 90 or 270	0	
$T_{\rm max}/\bar{T}_{\rm min}$	1.09	1.14	1.03	1.11	
Structure solution	Patterson synthesis yielded the Re positions, all remaining non-hydrogen atoms				
	were located via	standard Fourier te	chnique		
Atomic scattering factors ^c	Neutral atomic scattering factors were used throughout the analysis				
Anomalous dispersion ^d	Applied to all non-hydrogen atoms				
Final discrepancy factor	R = 0.070	0.070	0.050	0.066	
	$R_{w} = 0.070$	0.070	0.052	0.066	
Goodness of fit (GOF) ^f	1.337	1.369	1.172	1.496	

^a From a least-squares fitting of the setting angle of 25 reflections.

^bAll calculations were performed on a Data General Nova 3 computer with 32K of 16-bit words using local versions of the Nicolet SHELXTL interactive crystallographic software package as described in G. M. Sheldrick, Nicolet SHELXTL Operations Manual. Nicolet XRD, Cupertino, CA (1979).

^cD. T. Cromer and J. B. Mann, Acta Cryst. 1968, A24, 321.

^d International Tables for X-ray Crystallography, Vol. 3. Kynoch Press, Birmingham (1962).

 ${}^{e}R = \Sigma [|F_{o}| - |F_{c}|/\Sigma |F_{o}|], R_{w} = (\Sigma w(|F_{o}| - |F_{c}|)^{2}/\Sigma w|F_{o}|^{2}]^{1/2}, w = 1/\delta^{2}(F_{o}) + g^{*}(F_{o}), g = 0.0005.$ ${}^{f}GOF = [\Sigma w(|F_{o}| - |F_{c}|)^{2}/(N_{o} - N_{v})]^{1/2}, \text{ where } N_{o} \text{ is the number of observations and } N_{v} \text{ is the number of variables.}$

Materials and methods

All preparative reactions were performed in reagent grade solvents with no special precautions to eliminate atmospheric oxygen. [ReOCl₃(PPh₃)] was prepared by the literature method.²³ All other reagents were obtained from standard commercial sources and used without further purification.

The following instruments were used in this work: IR, Perkin-Elmer 283B IR spectrophotometer; X-ray crystallography, Nicolet R3m diffractometer.

All compounds were isolated as crystalline solids. Microanalytical data were obtained by MicAnal, Tucson, AZ.

Preparation of compounds

[ReCl(PPh₃)₂(NNC₆H₄Br-4)₂] (1). Oxotrichlorobis-(triphenylphosphine) rhenium (2.0 g), *p*-bromophenyl hydrazine hydrochloride (4.3 g) and triethylamine (15 cm³) were heated under reflux with stirring in 150 cm³ methanol for 30 min. The resulting red-brown solution is filtered, and the red precipitate washed with dry methanol, then air-dried giving 70% yield. Found : C, 51.3; H, 3.3; N, 5.0. Calc. for [ReCl(PPh₃)₂(NNC₆H₄Br)₂]: C, 51.7; H, 3.4; N, 5.0%.

[Re(SC₆H₃ - 2,5 - Me₂)(PPh₃)₂(NNC₆H₄Br - 4)₂] (2). Chlorobis(triphenylphosphine) bis(*p*-bromophenyldiazenido) rhenium (0.5 g), 2,5-dimethylthiophenol (0.43 g), and diisopropylethylamine (0.5 cm³) were warmed gently with stirring in benzene (150 cm³) overnight. The resulting deep red solution was filtered and the benzene removed by rotary evaporation. The red oil was dissolved in dichloromethane and layered with methanoldiethyl ether. Large red crystals form within 24 h. Found: C, 55.1; H, 3.9; N, 4.5. Calc. for [Re(SC₆H₃-2,5-Me₂)(PPh₃)₂(NNC₆H₄Br-4)₂]: C, 55.3; H, 3.9; N, 4.6%.

 $(PPh_4)[ReO(SPh)_4]$ (3). Was prepared by literature method with substitution of tetraphenyl phosphonium bromide for the arsonium salt.

[ReO(NNMePh)(SPh)₃] (4). (PPh₄)[ReO(SPh₄)] (1.0 g) 1,1-methylphenyl hydrazine (0.57 cm^3) and diisopropylethylamine (1.0 cm^3) were refluxed in 100 cm³ of methanol with stirring. The color gradually changed from purple-black to red, after which the solution is filtered. The methanol was removed by rotary evaporation giving a red oil. This material is redissolved in methanol and layered with diethyl ether, giving bright red-orange crystals. Found : C, 45.9; H, 3.5; N, 4.2. Calc. for ReO(NNMePh) $(SPh)_3$: C, 46.2; H, 3.6; N, 4.3%.

X-ray crystallography

The experimental details of the data collections and structure solutions are summarized in Table 4. A complete description of crystallographic protocols may be found in Ref. 24.

Final atomic positional and thermal parameters, bond lengths and angles and F_o/F_c values have been deposited as supplementary material with the Editor, from whom copies are available on request. Atomic coordinates have also been submitted to the Cambridge Crystallographic Data Centre.

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