Mono- and Bis-diazenido Complexes of Rhenium(III) containing Bidentate Ditertiary Phosphine Ligands. The Crystal and Molecular Structures of $[Re(NNC_6H_4Me\text{-}4)_2(Ph_2PCH_2CH_2PPh_2)_2][PF_6]\cdot 2dmf$, $[Re(NNC_6H_4Cl\text{-}4)_2(Me_2PCH_2CH_2PMe_2)_2][PF_6]$ and $[ReCl(NNC_6H_4Me\text{-}4)(Me_2PCH_2CH_2PMe_2)_2][PF_6]$†

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Reaction of the Re^{III} bis-diazenido starting materials $[ReCl(NNC_6H_4X\text{-}4)_2(PPh_3)_2]$ (X = Cl **1** or Me **2**) with excess dppe ($Ph_2PCH_2CH_2PPh_2$) in methanol–toluene under reflux gave the novel orange-brown, formally 20-electron Re^{III} bis-diazenido cations $[Re(NNC_6H_4X\text{-}4)_2(dppe)_2]^+$ (X = Cl or Me) in good yield by addition of a suitable anion to the cooled reaction mixture. Reaction of **1** and **2** with the more reducing dmpe ($Me_2PCH_2CH_2PMe_2$) ligand gave the formally 20-electron bis-diazenido cation $[Re(NNC_6H_4X\text{-}4)_2(dmpe)_2]^+$ for X = Cl but the 18-electron mono-diazenido cation $[ReCl(NNC_6H_4X\text{-}4)(dmpe)_2]^+$ for X = Me. The structures of complexes $[Re(NNC_6H_4Me\text{-}4)_2(dppe)_2][PF_6]\cdot 2dmf$ (dmf = dimethylformamide) **5**, $[Re(NNC_6H_4Cl\text{-}4)_2(dmpe)_2][PF_6]$ **6** and $[ReCl(NNC_6H_4Me\text{-}4)(dmpe)_2][PF_6]$ **7** have been determined: **5**, triclinic, space group $P\bar{1}$, $a = 13.046(3)$, $b = 13.250(3)$, $c = 12.233(4)$ Å, $\alpha = 110.74(2)$, $\beta = 95.86(2)$, $\gamma = 115.83(2)°$, $Z = 1$, $R = 0.040$; **6** monoclinic, space group $P2_1/c$, $a = 8.992(2)$, $b = 21.947(2)$, $c = 18.982(2)$ Å, $\beta = 91.45(1)°$, $Z = 4$, $R = 0.056$; **7** orthorhombic, space group $Pnma$, $a = 19.298(2)$, $b = 11.327(2)$, $c = 13.960(2)$ Å, $\alpha = \beta = \gamma = 90°$, $Z = 4$, $R = 0.042$. All three complexes have pseudo-octahedral co-ordination with four P donors in a planar equatorial array. The M–N–N angle of the diazenide ligands is found to be dependent on the steric requirements of the diphosphine ligands, the smaller dmpe ligand permitting the M–N–N angles in **6** to decrease to 147.3(5) and 149.0(4)° compared to values of around 162.7(2)° for the dppe complex **5**. Reaction of $[NH_4][ReO_4]$ with the arylhydrazine hydrochloride $4\text{-}MeC_6H_4NHNH_2\cdot HCl$ in CH_2Cl_2 in the presence of $SiMe_3Cl$ and pyridine (py) gave the new hydrazide $[ReCl_3\{NN(SiMe_3)C_6H_4Me\text{-}4\}_2(py)]$. Subsequent reaction with PPh_3 in MeOH gave the Re^{III} diazenide $[Re(OMe)(NNC_6H_4Me\text{-}4)_2(PPh_3)_2]$, and overall this provides a route for the synthesis of Re diazenides directly from perrhenate.

Monocationic technetium-99m complexes are useful myocardial perfusion agents in diagnostic nuclear medicine.[1] The close similarities between rhenium and technetium chemistry allows us to model the development of new cationic technetium radiopharmaceuticals for myocardial imaging in our laboratories using the non-radioactive rhenium. This work is also of interest in the development of therapeutic rhenium radiopharmaceuticals based on the ^{186}Re and ^{188}Re isotopes. We have recently reported the high yield synthesis of monocationic technetium complexes containing bis- and monodiazenido cores from the common starting material $[NBu_4][TcOCl_4]$ and also directly from $[NH_4][TcO_4]$, the chemical form of technetium used in commercial radiopharmaceutical synthesis.[2]

The present study involves an investigation of a number of cationic mono- and bis-diazenido complexes of rhenium(III) with the bidentate ditertiary phosphine ligands, 1,2-bis(diphenylphosphino)ethane (dppe) and 1,2-bis(dimethylphosphino)ethane (dmpe). We are particularly interested in the subtle differences in the steric and electronic environment of these ligands on the bonding modes and geometries of the N_2R ligand. We also include details of a route to Re diazenides directly from perrhenate, which is significant in the context of the development of potential radiopharmaceuticals for which perrhenate is the only viable precursor.

Results and Discussion

We have already shown that the reaction of $[ReOCl_3(PPh_3)_2]$ with the monosubstituted arylhydrazines $4\text{-}X\text{-}C_6H_4NHNH_2$ leads to the formation of the neutral orange 18-electron Re^{III} bis-diazenido complexes $[ReCl(NNC_6H_4X\text{-}4)_2(PPh_3)_2]$ (X = Cl or Me).[3] By contrast a monodiazenide complex $[ReCl_2(NNC_6H_4NO_2\text{-}4)(PPh_3)_2]$ is formed using the 4-nitro-substituted arylhydrazine. This is a further example of the considerable effects exerted by substituents on the aromatic ring and probably reflects changes in the pK_a values of the hydrazinic protons.

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Table 1 Analytical and spectroscopic data for rhenium diazenido complexes

Complex	Colour, yield (%)	Analysis[a] (%) C	H	N	IR[b] (cm^{-1}) ν(N=N)	^{31}P NMR[c] (δ)
[ReCl(NNC$_6$H$_4$Cl-4)$_2$(PPh$_3$)$_2$] **1**	Dark red, 51	55.8	3.7	5.4	1510 (1545)	29.9 (s)
		(56.2)	(3.7)	(5.5)		
[ReCl(NNC$_6$H$_4$Me-4)$_2$(PPh$_3$)$_2$] **2**	Dark orange, 50	60.6	4.3	5.4	1580 (1630)	23.9 (s)
		(61.0)	(4.5)	(5.7)		
[ReCl$_2$(NNC$_6$H$_4$NO$_2$-4)(PPh$_3$)$_2$] **3**	Brown-black, 67	54.2	3.4	4.3	1515 (1565)	30.0 (s)
		(54.1)	(3.7)	(4.5)		
[Re(NNC$_6$H$_4$Cl-4)$_2$(dppe)$_2$][BPh$_4$] **4**	Bright red, 44	67.2	4.9	3.5	1520 (1580)	10.4 (br s)
		(66.8)	(5.0)	(3.5)		
[Re(NNC$_6$H$_4$Me-4)$_2$(dppe)$_2$][PF$_6$]·2dmf **5**	Magenta, 29	58.4	5.0	4.5	1525 (1575)	—
		(59.0)	(5.2)	(4.8)		
[Re(NNC$_6$H$_4$Cl-4)$_2$(dmpe)$_2$][PF$_6$] **6**	Magenta, 93	30.7	4.4	5.8	1570 (1585)	20.7 (br s)
		(31.7)	(4.4)	(6.2)		
[ReCl(NNC$_6$H$_4$Me-4)(dmpe)$_2$][PF$_6$] **7**	Maroon, 98	28.6	4.7	3.2	—	—
		(29.0)	(5.0)	(3.6)		
[ReCl$_2$(NNC$_6$H$_4$NO$_2$-4)(dppe)(PPh$_3$)] **8**	Dark orange, 55	63.7	3.9	3.8	1573	30.6 (d),
		(64.2)	(4.1)	(4.0)		34.1 (t)
[ReCl$_2$(NNC$_6$H$_4$NO$_2$-4)(dmpe)$_2$] **9**	Dark purple, 79	31.3	5.1	6.5	1585	6.33 (s)
		(30.6)	(5.1)	(5.9)		
[Re(OMe)(NNC$_6$H$_4$Me-4)$_2$(PPh$_3$)$_2$]·CH$_2$Cl$_2$	Orange, 62	58.3	4.3	4.8	1555 (1613)	−4.6 (s)
		(58.6)	(4.6)	(5.2)		
[ReCl$_3${NN(SiMe$_3$)C$_6$H$_4$Me-4}$_2$(py)]·CH$_2$Cl$_2$[d]	Brown, 29.5	38.8	3.9	8.8	1608	—
		(38.7)	(4.8)	(8.7)		

[a] Calculated values in parentheses. [b] As Nujol mulls (KBr plates). [c] In CDCl$_3$ solution, s = singlet, d = doublet, t = triplet br = broad. [d] Cl, found 10.7; calc. 10.0 %.

We have now found that the related alkoxide complex [Re(OMe)(NNC$_6$H$_4$Me-4)$_2$(PPh$_3$)$_2$] can be prepared in a straightforward method directly from perrhenate. Reaction of [NH$_4$][ReO$_4$] with 4-tolylhydrazine hydrochloride in reagent grade dichloromethane in the presence of SiMe$_3$Cl and pyridine gives the novel bis-hydrazide [ReCl$_3${NN(SiMe$_3$)C$_6$H$_4$Me-4}$_2$(py)] (py = pyridine) as a brown somewhat moisture sensitive solid. This shows IR bands at 1608 and 850 cm^{-1} assigned to ν(N=N) and the SiMe$_3$ groups respectively (see Table 1). In the ^{1}H NMR spectrum the SiMe$_3$ groups give rise to two sharp singlets close to δ 0 and the 4-tolyl groups appear as two singlets at δ 2.3 and 2.7, indicating that the hydrazides are in inequivalent environments. The FAB mass spectrum of the complex shows an ion at 926 corresponding to the complex minus one SiMe$_3$ group, and has an appropriate isotope distribution. This complex is directly analogous to the complexes [ReCl$_3$(NNR$_2$)$_2$(py)] prepared under similar conditions from the appropriate 1,1-disubstituted hydrazines.[4] Reaction of [ReCl$_3${NN(SiMe$_3$)C$_6$H$_4$Me-4}$_2$(py)] with triphenylphosphine in methanol generates the new alkoxy diazenide complex [Re(OMe)(NNC$_6$H$_4$Me-4)$_2$(PPh$_3$)$_2$] in good yield. This complex shows the expected singlets in the ^{1}H NMR spectrum for the methoxy and equivalent 4-methyl groups of the diazenide groups and a singlet in the ^{31}P NMR indicative of equivalent phosphorus ligands. The structure is therefore presumably directly analogous to the structurally characterised chloro 4-chlorophenyldiazenide derivative **1** with equatorial methoxide and diazenide groups and axial phosphine ligands.

The neutral Re^{III} bis-diazenido complexes [ReCl(NNC$_6$H$_4$-X-4)$_2$(PPh$_3$)$_2$] (X = Cl **1** or Me **2**) react with excess dppe in methanol–toluene (1:1) under reflux to give red-orange crystalline bis-diazenido cations of the type [Re(NNC$_6$H$_4$X-4)$_2$(dppe)$_2$]$^+$ which are readily precipitated from solution by addition of a suitable anion. This rhenium chemistry is in contrast to the recently reported high yield syntheses of technetium mono-diazenido cations [TcCl(NNC$_6$H$_4$X-4)(dppe)$_2$]$^+$ (X = H, Cl or Me) either directly from [NBu$_4$][TcOCl$_4$] or [NH$_4$][TcO$_4$], dppe and the corresponding arylhydrazine, or by substitution of the technetium bis-diazenido starting materials [TcCl(NNC$_6$H$_4$X-4)$_2$(PPh$_3$)$_2$] with dppe.[2] Reaction of the technetium bis-diazenido starting materials to give the mono-diazenido cations suggests that for technetium, one of the hydrazine-derived ligands is much more labile than the other, and is lost upon reaction with the dppe ligand. Apparently, these rhenium complexes are able to sustain the two N$_2$R ligands under these reaction conditions to give the complexes [Re(NNR)$_2$(dppe)$_2$]$^+$. These have a formal valence count of 20 electrons if each diazenide ligand is assumed to donate three electrons* to the metal.

The rhenium(III) bis-diazenido cations are readily soluble in CH$_2$Cl$_2$ and CHCl$_3$, but are insoluble in alcohols and alkanes. The complexes exhibit bands in the IR spectrum between 1510 and 1585 cm^{-1} which are assigned to ν(N=N).

The orange mono-diazenido complex [ReCl$_2$(NNC$_6$H$_4$-NO$_2$-4)(PPh$_3$)$_2$] **3** reacts with excess dppe under methanol–toluene reflux to give a neutral dark orange-brown complex formulated as [ReCl$_2$(NNC$_6$H$_4$NO$_2$-4)(dppe)(PPh$_3$)] **8**.

The reaction of the bis-diazenido starting materials and **2** with the smaller, more electron-rich dmpe ligand in excess gave the expected bis-diazenido cationic complex [Re(NNC$_6$H$_4$X-4)$_2$(dmpe)$_2$]$^+$ for X = Cl, but gave a mono-diazenido cation, [ReCl(NNC$_6$H$_4$X-4)(dmpe)$_2$]$^+$ for X = Me. This is a further example of the significant effects exerted by substituents in the 4-position of the aryldiazenido complexes (see above).

The reaction of complex **3** with excess dmpe in methanol–toluene under reflux gave the neutral mono-diazenido complex [ReCl$_2$(NNC$_6$H$_4$NO$_2$-4)(dmpe)$_2$] **9**. The elemental analysis and conductivity measurements support the formulation as a neutral complex. The formation of the neutral rather than cationic complex is a further example of anomalous chemistry for the 4-nitro-substituted complex. The singlet observed in the ^{31}P NMR spectrum shows the P donors are all equivalent,

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* This formalism is dependent on the convention adopted to count valence electrons. We here assume the metal to be in the zero oxidation state (seven electrons) with the bidentate phosphines contributing four each. If the metal is counted as trivalent (four electrons) the diazenides will each formally contribute four electrons.

Table 2 Positional parameters for $[\mathrm{Re(NNC_6H_4Me\text{-}4)_2(dppe)_2][PF_6]\cdot 2dmf}$ **5**

Atom	*x*	*y*	*z*
Re	0.500	0.500	0.500
P(1)	0.473 76(7)	0.463 14(7)	0.285 79(7)
P(2)	0.684 67(7)	0.492 89(7)	0.479 68(7)
P(3)	0.500	0.000	0.000
F(1)	0.448 6(6)	−0.020 4(5)	0.102 5(4)
F(2)	0.613 2(6)	0.009 0(5)	0.062 8(7)
F(3)	0.437 3(5)	−0.143 7(4)	−0.074 0(5)
O	1.023(1)	0.432(1)	−0.097(1)
N(1)	0.420 9(2)	0.321 9(2)	0.432 2(2)
N(2)	0.386 9(3)	0.211 8(2)	0.366 6(3)
N(3)	0.853 8(6)	0.368 1(6)	0.068 4(6)
C(1)	0.562 5(3)	0.391 1(3)	0.230 9(3)
C(2)	0.689 0(3)	0.467 1(3)	0.321 4(3)
C(3)	0.285 9(3)	0.111 6(3)	0.372 6(3)
C(4)	0.329 6(3)	0.351 2(3)	0.166 8(3)
C(5)	0.526 1(3)	0.598 8(3)	0.254 5(3)
C(6)	0.836 6(3)	0.623 2(3)	0.567 1(3)
C(7)	0.692 9(3)	0.363 2(3)	0.493 3(3)
C(31)	0.236 4(4)	0.123 2(3)	0.467 6(4)
C(32)	0.139 1(4)	0.018 5(4)	0.461 1(4)
C(33)	0.086 9(4)	−0.098 0(3)	0.359 6(4)
C(34)	0.138 4(4)	−0.107 1(3)	0.266 9(4)
C(35)	0.239 0(4)	−0.005 2(3)	0.272 7(4)
C(41)	0.286 0(4)	0.221 5(3)	0.119 3(3)
C(42)	0.176 1(4)	0.136 7(4)	0.029 2(4)
C(43)	0.108 5(4)	0.177 6(4)	−0.013 6(5)
C(44)	0.149 6(4)	0.304 4(4)	0.031 8(5)
C(45)	0.259 6(4)	0.390 1(3)	0.121 9(4)
C(51)	0.499 4(4)	0.691 0(3)	0.312 9(4)
C(52)	0.529 0(4)	0.790 7(3)	0.285 0(4)
C(53)	0.589 1(5)	0.801 7(4)	0.200 0(4)
C(54)	0.619 6(5)	0.713 4(4)	0.143 6(4)
C(55)	0.587 1(4)	0.610 8(4)	0.168 5(4)
C(61)	0.859 9(4)	0.735 5(3)	0.658 5(4)
C(62)	0.976 7(4)	0.834 9(4)	0.718 4(5)
C(63)	1.070 7(4)	0.822 0(5)	0.687 9(5)
C(64)	1.048 9(4)	0.710 1(4)	0.598 6(5)
C(65)	0.933 0(4)	0.611 1(4)	0.538 1(4)
C(71)	0.632 7(3)	0.243 7(3)	0.395 6(4)
C(72)	0.633 7(4)	0.144 6(3)	0.410 8(5)
C(73)	0.693 8(4)	0.163 3(3)	0.521 5(5)
C(74)	0.756 5(4)	0.282 5(4)	0.617 8(4)
C(75)	0.757 1(3)	0.382 2(3)	0.604 0(4)
C(80)	0.962(1)	0.483(1)	0.130(1)
C(81)	0.849 1(9)	0.262 0(9)	0.085 2(9)
C(82)	0.754(1)	0.351 9(9)	−0.015(1)

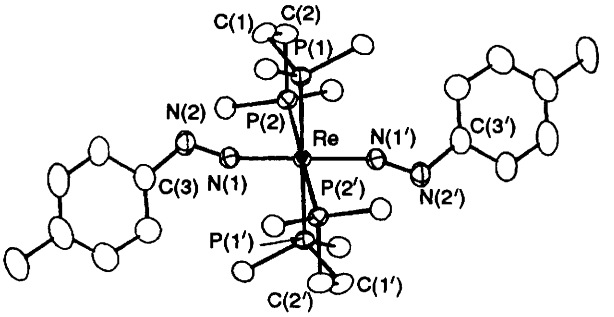

Fig. 1 An ORTEP view of the structure of the cation of complex **5** showing a partial atom labelling scheme. Only the aryl carbons attached to phosphorus are shown for clarity

suggesting a structure where all four P donors lie in a plane. Unfortunately we were unable to obtain suitable crystals for absolute structural confirmation by X-ray crystallography.

In an attempt to delineate further the differences in bonding of the diazenide ligands created by the different diphosphines, we have determined the structures of complexes **5**, **6** and **7**.

X-Ray Crystal Structures of Complexes **5**, **6** *and* **7**.—The molecular structures of the cations of complexes **5**, **6** and **7** are represented in Figs. 1, 2 and 3 respectively. Positional parameters and selected bond angles and distances are given in Tables 2–7.

For complex **5** which incorporates two molecules of dimethylformamide (dmf), the overall geometry about $\mathrm{Re^{III}}$ is pseudo-octahedral, and the molecule has a centre of symmetry. The phosphorus atoms of the two dppe ligands occupy four equatorial co-ordination sites and the $\mathrm{N_2R}$ ligands occupy the *trans*-axial positions. The bidentate co-ordination of the two equatorial dppe ligands results in two five-membered chelate rings about the rhenium centre. The Re–N(1)–N(2) angle is 162.7(2)° indicating that the $\mathrm{N_2R}$ ligands are formally acting as three-electron donors (see footnote* on previous page). This confers an overall formal 20-electron valence configuration on the transition metal. The Re–N(1) distance of 1.909(2) Å is significantly longer than the normal distances of 1.75–1.80 Å found for $\mathrm{N_2R}$ complexes[5] and reflects competition for suitable metal orbitals by the *trans*-diazenide ligands

Table 3 Selected bond distances (Å) and angles (°) for complex **5**

Re–P(1)	2.4469(7)	N(1)–N(2)	1.223(3)
Re–P(2)	2.4863(7)	N(2)–C(3)	1.432(4)
Re–N(1)	1.909(2)		
P(1)–Re–P(1')	180	P(2)–Re–N(1)	93.87(7)
P(1)–Re–P(2)	98.26(2)	P(2)–Re–N(1')	86.14(7)
P(1)–Re–P(2')	81.74(2)	N(1)–Re–N(1')	180
P(1)–Re–N(1)	84.24(7)	Re–N(1)–N(2)	162.7(2)
P(1)–Re–N(1')	95.76(7)	N(1)–N(2)–C(3)	121.5(3)
P(2)–Re–P(2')	180		

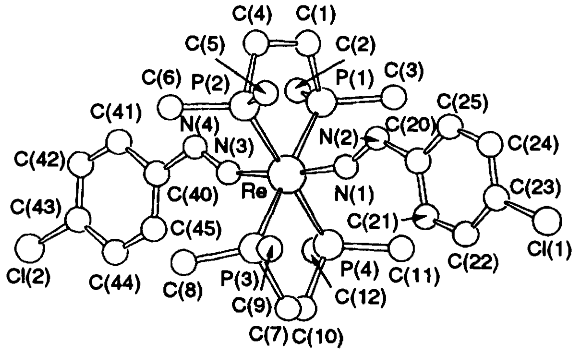

Fig. 2 Representation of the structure of the cation of complex **6** with the atom labelling scheme

The geometry about the Re in complex **6** is again approximately octahedral. The four phosphorus atoms of the two bidentate dmpe ligands occupy the four equatorial co-ordination sites with the two $-\mathrm{N_2R}$ ligands occupying mutually *trans*-axial positions. The Re–N(1)–N(2) and Re–N(3)–N(4) angles of 147.3(5) and 149.0(4)° respectively suggest that the $-\mathrm{N_2R}$ ligands are moving towards a geometry where they contribute one electron to the metal. It appears that the smaller diphosphine dmpe offers no steric hindrance towards the diazenide ligands bending at the α-nitrogen. The diazenide ligands apparently adjust their bonding to reduce the formal electron count at the metal, but do so symmetrically rather than adopting three (singly bent) and one (doubly bent) electron-donor forms. Moreover, the M–N distances for **6** are

Table 4 Positional parameters for $[Re(NNC_6H_4Cl\text{-}4)_2(dmpe)_2][PF_6]$ **6**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Re	0.204 52(6)	0.149 49(2)	0.228 19(3)	C(4)	0.200(2)	0.235(1)	0.077 7(9)
Cl(1)	0.876 5(5)	−0.112 5(2)	0.153 8(3)	C(5)	0.493(2)	0.223 6(8)	0.128(1)
Cl(2)	−0.410 6(5)	0.363 1(2)	0.450 6(2)	C(6)	0.295(2)	0.307 3(7)	0.190(1)
P(1)	0.057 3(4)	0.132 1(2)	0.122 3(2)	C(7)	0.315(2)	0.105(1)	0.394 8(9)
P(2)	0.304 9(4)	0.230 5(2)	0.158 2(2)	C(8)	0.336(2)	0.233 4(9)	0.382 9(9)
P(3)	0.358 0(4)	0.164 4(2)	0.333 4(2)	C(9)	0.560(2)	0.159 2(9)	0.324 6(9)
P(4)	0.103 2(4)	0.068 9(2)	0.299 1(2)	C(10)	0.182(2)	0.074 0(9)	0.387 3(8)
P(5)	0.238 1(8)	0.625 7(3)	0.958 2(3)	C(11)	0.139(2)	−0.008 5(7)	0.272 0(9)
F(1)	0.149(2)	0.642 9(7)	1.022 8(7)	C(12)	−0.098(2)	0.070 5(8)	0.315(1)
F(2)	0.377(2)	0.659 2(8)	0.990 5(8)	C(20)	0.521(1)	0.031 0(5)	0.145 5(7)
F(3)	0.200(2)	0.687 8(7)	0.925 9(8)	C(21)	0.560(1)	0.003 0(6)	0.208 6(7)
F(4)	0.327(2)	0.610 8(9)	0.891 4(7)	C(22)	0.668(2)	−0.041 2(6)	0.211 1(8)
F(5)	0.109(2)	0.593 0(8)	0.927(1)	C(23)	0.739(2)	−0.057 1(6)	0.149 7(8)
F(6)	0.298(3)	0.566 3(8)	0.990(1)	C(24)	0.703(2)	−0.029 9(6)	0.087 8(7)
N(1)	0.350(1)	0.095 9(4)	0.188 7(5)	C(25)	0.596(2)	0.014 2(6)	0.085 5(7)
N(2)	0.410(1)	0.077 1(5)	0.135 6(5)	C(40)	−0.117(1)	0.273 3(5)	0.294 2(6)
N(3)	0.056(1)	0.207 1(4)	0.255 9(5)	C(41)	−0.210(2)	0.320 3(6)	0.272 6(8)
N(4)	−0.030(1)	0.247 1(5)	0.239 9(5)	C(42)	−0.299(2)	0.348 4(6)	0.321 5(8)
C(1)	0.136(2)	0.179 8(9)	0.053 2(9)	C(43)	−0.296(2)	0.328 5(6)	0.390 0(7)
C(2)	−0.139(2)	0.151 0(9)	0.122 4(9)	C(44)	−0.204(2)	0.281 5(6)	0.412 2(7)
C(3)	0.059(2)	0.057 2(8)	0.082 7(8)	C(45)	−0.115(1)	0.254 3(6)	0.363 2(7)

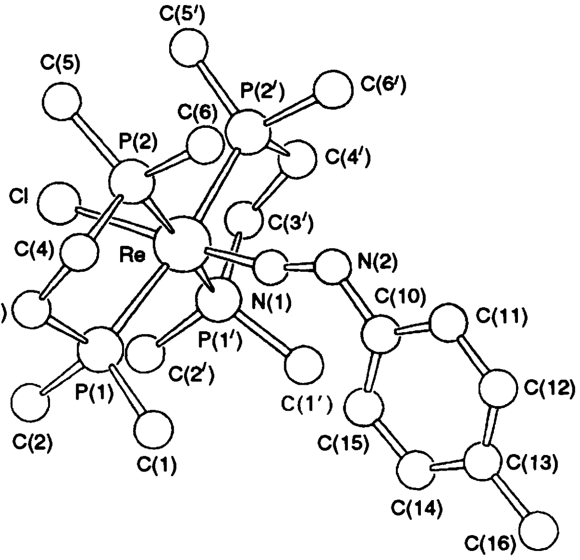

Fig. 3 Representation of the structure of the cation of complex **7** with the atom labelling scheme

much longer than those in complex **7** consistent with the diazenides acting as weaker π donors, and the formal electron count at the metal may be closer to 18. It is also noteworthy that the Re–N distances in **5** and **6** are similar although there is a dramatic difference in the Re–N–N angles. This strongly supports the idea that distortions of the M–N–N angles involve relatively small energy terms. The Re–P distances are similar in the two complexes and also to the values found for other rhenium diphosphine complexes.[6]

A summary comparison of the important structural data for complexes **5**, **6** and **7** is given in Table 8.

The Re^{III} atom in complex **7** lies once more in a distorted octahedral environment with the four phosphorus atoms in the equatorial co-ordination sites and the chloro group and the $-N_2R$ ligand are disposed mutually *trans*. The Re–Cl bond length of 2.463(2) Å is comparable with values for other Re^{III} complexes, and confirms that the diazenide ligand exerts a negligible *trans* influence. Doubly bent N_2R ligands can exert a much stronger *trans* influence on mutually *trans*-disposed ligands such as halide.[7]

Table 5 Selected bond lengths (Å) and angles (°) for complex **6**

Re–P(1)	2.409(2)	Re–N(3)	1.920(4)
Re–P(2)	2.410(2)	N(1)–N(2)	1.224(6)
Re–P(3)	2.421(1)	N(3)–N(4)	1.204(6)
Re–P(4)	2.415(2)	N(2)–C(20)	1.429(7)
Re–N(1)	1.928(4)	N(4)–C(40)	1.433(7)
P(1)–Re–P(2)	82.10(6)	P(3)–Re–N(1)	91.4(1)
P(1)–Re–P(3)	178.17(6)	P(3)–Re–N(3)	94.1(1)
P(1)–Re–P(4)	98.16(6)	P(4)–Re–N(1)	92.3(1)
P(1)–Re–N(1)	86.8(1)	P(4)–Re–N(3)	93.2(1)
P(1)–Re–N(3)	87.8(1)	N(1)–Re–N(3)	172.8(2)
P(2)–Re–P(3)	98.13(6)	Re–N(1)–N(2)	147.3(5)
P(2)–Re–P(4)	179.51(6)	Re–N(3)–N(4)	149.0(4)
P(2)–Re–N(1)	88.1(1)	N(1)–N(2)–C(20)	116.6(5)
P(2)–Re–N(3)	86.5(1)	N(3)–N(4)–C(40)	118.2(5)
P(3)–Re–P(4)	81.64(6)		

Experimental

Infrared spectra were recorded on a Perkin-Elmer 257 spectrophotometer and NMR spectra on a Bruker WP-80 NMR spectrometer with synthesiser frequencies of 80.13 and 32.44 MHz for ^1H and $^{31}P\text{-}\{^1H\}$ respectively. Elemental analyses were performed by Butterworth Laboratories Ltd, Teddington, Middlesex, UK, and HPLC analyses using a Gilson model 702 isocratic HPLC system fitted with a polystyrene–divinylbenzene copolymer column and an HM Holochrome UV detection module (set at 250 nm). An elution gradient between tetrahydrofuran and aqueous 0.01 mol dm^{-3} tetra-*n*-butylammonium bromide was controlled by an Apple II-C microcomputer.

Unless otherwise stated, starting materials were purchased from Aldrich and used without further purification. 1,2-Bis(diphenylphosphino)ethane was prepared and purified by literature methods.[8]

Preparation of the Complexes—The dark orange-red crystalline bis-diazenido rhenium(III) starting materials $[ReCl(NNC_6H_4X\text{-}4)_2(PPh_3)_2]$ (X = Cl **1** or Me **2**) and the brown-black rhenium(III) monodiazenido complex $[ReCl_2(NNC_6H_4NO_2\text{-}4)(PPh_3)_2]$ **3** were prepared in 50–70% yield from $[ReOCl_3(PPh_3)_2]$[9] and the corresponding arylhydrazine, $4\text{-}NO_2C_6H_4NHNH_2$ or arylhydrazine hydrochloride, $4\text{-}XC_6H_4NHNH_2{\cdot}HCl$ (X = Cl or Me), and triethylamine in dry methanol under nitrogen reflux according to the published

Table 6 Positional parameters for $[ReCl(NNC_6H_4Me\text{-}4)(dmpe)_2][PF_6]$ **7**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Re	0.071 53(2)	0.250	0.205 42(3)	C(2)	−0.096 7(5)	0.092(1)	0.234 7(9)
Cl	0.002 3(2)	0.250	0.057 3(3)	C(3)	0.021 4(5)	−0.044(1)	0.183 3(9)
P(1)	−0.002 4(1)	0.087 1(3)	0.254 1(2)	C(4)	0.102 6(6)	−0.053(1)	0.178(1)
P(2)	0.137 8(1)	0.088 4(3)	0.137 5(2)	C(5)	0.142 2(6)	0.075(1)	0.007 0(7)
P(3)	0.146 5(2)	0.750	0.443 1(3)	C(6)	0.228 7(5)	0.073(1)	0.175 8(8)
F(1)	0.224 9(6)	0.750	0.473(1)	C(10)	0.169 4(7)	0.250	0.463 5(8)
F(2)	0.130(1)	0.750	0.548 9(9)	C(11)	0.231 8(7)	0.250	0.515 1(9)
F(3)	0.165 9(9)	0.750	0.336(1)	C(12)	0.228 2(7)	0.250	0.615 8(9)
F(4)	0.071 3(5)	0.750	0.410(1)	C(13)	0.165 6(7)	0.250	0.663 9(8)
F(5)	0.146 4(6)	0.616 2(9)	0.441(1)	C(14)	0.105 4(7)	0.250	0.610 3(9)
N(1)	0.127 2(5)	0.250	0.307 5(6)	C(15)	0.106 4(6)	0.250	0.510 2(8)
N(2)	0.177 2(5)	0.250	0.362 3(7)	C(16)	0.163 3(9)	0.250	0.772 6(9)
C(1)	0.004 4(7)	0.042(1)	0.379 5(7)				

Table 7 Selected bond distances (Å) and angles (°) for complex **7**

Re–Cl	2.463(2)	Re–N(1)	1.784(5)
Re–P(1)	2.429(1)	N(1)–N(2)	1.233(7)
Re–P(2)	2.427(1)	N(2)–C(10)	1.420(7)
Cl–Re–P(1)	85.21(4)	P(1)–Re–P(2′)	172.75(5)
Cl–Re–P(1′)	85.20(4)	P(1)–Re–N(1)	97.5(2)
Cl–Re–P(2)	87.58(4)	P(2)–Re–P(2′)	97.97(7)
Cl–Re–P(2′)	87.59(4)	P(2)–Re–N(1)	89.8(2)
Cl–Re–N(1)	175.9(2)	Re–N(1)–N(2)	165.4(4)
P(1)–Re–P(1′)	98.85(7)	N(1)–N(2)–C(10)	122.4(5)
P(1)–Re–P(2)	81.13(5)		

Table 8 Comparison of selected bond angles and distances for **5**, **6** and **7**

Complex	Re–N–N/°	Re–N/Å	N–N/Å	Re–P (av.)/Å
5	162.7(2)	1.909(2)	1.223(3)	2.467
6	147.3(5)	1.928(4)	1.224(6)	2.414
	149.0(4)	1.920(4)	1.204(6)	
7	165.4(4)	1.784(5)	1.233(7)	2.428

procedure.[3] Analytical and spectroscopic data for the new complexes and the following compounds are given in Table 1.

$[Re(NNC_6H_4Cl\text{-}4)_2(dppe)_2][BPh_4]$ **4**. Complex **1** (0.7 g, 0.68 mmol) and dppe (1.44 g, 361 mmol) were heated under reflux in dry methanol–toluene (1 : 1, 10 cm^3) for 2 h to give a dark orange-red solution. Solid $NaBPh_4$ (0.5 g, 1.46 mmol) was added with stirring to the cooled reaction mixture to precipitate the product. A bright red solid was recrystallised from CH_2Cl_2–MeOH (yield 0.47 g, 44%).

$[Re(NNC_6H_4Me\text{-}4)_2(dppe)_2][PF_6]\cdot 2dmf$ **5**. Complex **2** (0.55 g, 0.57 mmol) and dppe (0.55 g, 1.4 mmol) were heated under reflux in dry methanol–toluene (1 : 1, 10 cm^3) for 2 h to give a dark red solution. Solid $[NBu_4][PF_6]$ (0.2 g, 0.604 mmol) was added with stirring to the cooled reaction mixture to precipitate the product. Magenta needle-like crystals of **5** were obtained from dmf–propan-2-ol (yield 0.16 g, 29%).

$[Re(NNC_6H_4Cl\text{-}4)_2(dmpe)_2][PF_6]$ **6**. Complex **1** (0.21 g, 0.204 mmol) and dmpe (0.12 cm^3, 0.8 mmol) were heated under reflux in dry methanol–toluene (1 : 1, 10 cm^3) for 2 h to give a deep red solution. Solid $[NBu_4][PF_6]$ (0.2 g, 0.604 mmol) was added with stirring to the cooled reaction mixture to precipitate the product. Magenta needle-like crystals were recrystallised from CH_2Cl_2–propan-2-ol (yield 0.16 g, 93%).

$[ReCl(NNC_6H_4Me\text{-}4)(dmpe)_2][PF_6]$ **7**. Complex **2** (0.20 g, 0.203 mmol) and dmpe (0.08 cm^3, 0.508 mmol) were heated under reflux in dry methanol–toluene (1 : 1, 4 cm^3) for 2 h to give a deep red solution. Solid $[NH_4][PF_6]$ (0.11 g, 0.675 mmol) was added with stirring to the cooled reaction mixture to precipitate the product. A maroon solid was recrystallised from CH_2Cl_2–Et_2O (yield 0.15 g, 98%).

$[ReCl_2(NNC_6H_4NO_2\text{-}4)(dppe)(PPh_3)]$ **8**. Complex **3** (0.72 g, 0.77 mmol) and dppe (0.69 g, 1.72 mmol) were heated under reflux in dry methanol–toluene (1 : 1, 10 cm^3) for 2 h. Upon cooling the dark brown mixture a dark orange-brown solid precipitated (yield 0.45 g, 55%).

$[ReCl_2(NNC_6H_4NO_2\text{-}4)(dmpe)_2]$ **9**. Complex **3** (0.35 g, 0.37 mmol) and dmpe (0.07 cm^3, 0.42 mmol) were heated under reflux in dry methanol–toluene (1 : 1, 2 cm^3) for 2 h. On cooling a deep red-purple fine suspension was obtained which resisted attempts at filtration. This was evaporated to dryness *in vacuo* and the residue recrystallised from CH_2Cl_2–Et_2O to give a dark purple solid (yield 0.21 g, 79%).

$[ReCl_3\{NN(SiMe_3)C_6H_4Me\text{-}4\}_2(py)]$. 4-Methylphenylhydrazinium chloride (0.53 g, 3.36 mmol) and pyridine (0.9 cm^3) were added to a suspension of ammonium perrhenate (0.3 g, 1.12 mmol) in dichloromethane (10 cm^3). The mixture was cooled to −40 °C, and trimethylchlorosilane (1.10 cm^3, 8.67 mmol) added quickly dropwise. The reaction mixture was then stirred at room temperature for 1 h to give a dark purple solution. The solvent was removed *in vacuo* and the dark residue extracted with boiling toluene. On cooling dark brown crystals of the complex precipitated (yield 0.25 g, 29.5%).

$[Re(OMe)(NNC_6H_4Me\text{-}4)_2(PPh_3)_2]$. The complex $[ReCl_3\{NN(SiMe_3)C_6H_4Me\text{-}4\}_2(py)]$ (0.1 g, 0.18 mmol) and PPh_3 (0.14 g, 0.53 mmol) in methanol (10 cm^3) were heated under reflux for 20 min. On cooling an orange powder precipitated from the dark orange solution. This was filtered, washed with diethyl ether and dried *in vacuo* (yield 0.12 g, 62%).

Crystal Structure Determinations.—All X-ray experiments were carried out at 18 °C on a single-crystal CAD 4 diffractometer with Cu-Kα (complexes **6** and **7**) or Mo-Kα (complex **5**) radiation. The lattice parameters were refined using 25 reflections of high diffraction angles. Intensity data were performed for the asymmetric unit of the reciprocal lattice with omega–theta scans. Direct methods[10] and subsequent Fourier difference syntheses were used for the solution of the structures. After an empirical absorption correction (DIFABS)[11] the structures were refined[12] with anisotropic thermal parameters for all non-hydrogen atoms. The positions of the hydrogen atoms were calculated but not included in the refinement. Further details of the structure determinations are given in Table 9.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters and remaining bond lengths and angles.

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Table 9 Details of crystal structure determinations *

Compound	$[Re(NNC_6H_4Me\text{-}4)_2(dppe)_2][PF_6]\cdot 2dmf$ **5**	$[Re(NNC_6H_4Cl\text{-}4)_2(dmpe)_2][PF_6]$ **6**	$[ReCl(NNC_6H_4Me\text{-}4)(dmpe)_2][PF_6]$ **7**
Formula	$C_{66}H_{62}F_6N_4P_5Re\cdot 2C_3H_7NO$	$C_{24}H_{40}Cl_2F_6N_4P_5Re$	$C_{19}H_{39}ClF_6N_2P_5Re$
M	1512.51	910.58	786.05
a/Å	13.046(3)	8.992(2)	19.298(2)
b/Å	13.250(3)	21.947(2)	11.327(2)
c/Å	12.233(4)	18.982(2)	13.960(2)
α/°	110.74(2)		
β/°	95.86(2)	91.45(1)	
γ/°	115.83(2)		
U/Å^3	1695.4	3744.7	3051.2
Z	1	4	4
D_c/g cm^{-3}	1.481	1.615	1.711
$F(000)$	770	1800	1552
Crystal system	Triclinic	Monoclinic	Orthorhombic
Space group	$P\bar{1}$	$P2_1/c$	$Pnma$
Radiation	Mo-Kα (graphite monochromator)	Cu-Kα	Cu-Kα
Crystal size/mm	0.45 × 0.25 × 0.15	0.35 × 0.20 × 0.10	0.30 × 0.20 × 0.15
Theta range/°	3–30	5–60	5–65
Index range	$0 < h < 18, -18 < k < 18, -17 < l < 17$	$0 < h < 10, 0 < k < 25, -22 < l < 22$	$0 < h < 7, 0 < k < 16, 0 < l < 22$
Reflections collected	10 256	6092	2117
Observed reflections ($I > 3\sigma I$)	9147	4200	1909
Absorption coefficient/cm^{-1}	19,960	99,963	113,264
Absorption correction, K_{min}, K_{max}	0.839, 1.072	0.828, 1.774	0.725, 1.303
Refined parameters	394	380	178
Secondary extinction coefficient	$1.155\,40 \times 10^{-8}$	2.2675×10^{-8}	No extinction correction
Maximum, minimum electron density, $10^6 \rho$/e pm^{-3}	1.49, −1.04	2.033, −2.541	0.901, −0.622
R, R'	0.040, 0.046	0.056, 0.066	0.042, 0.048

* Details in common: Enraf-Nonius CAD 4 diffractometer, ω–θ scan method, T = 18 °C, weighting scheme $w = 1/\sigma^2$.

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