Rhenium Complex of a Triply Deprotonated Chelated Thiosemicarbazide and its Conversion to a Nitride Complex *via* a Hydrazide Intermediate. Crystal Structure of $[ReCl_2(NH)(NHNH_2)(PPh_3)_2]$†

Jonathan R. Dilworth,* Jason S. Lewis, John R. Miller and Yifan Zheng
Department of Chemistry and Biological Chemistry, University of Essex, Wivenhoe Park, Colchester CO4 3SQ, UK

Reaction of $[Re(O)X_3(PPh_3)_2]$ (X = Cl or Br) with thiosemicarbazides $RNHCSNHNH_2$ (R = Me or Ph) in ethanol under reflux in the presence of aqueous HX and PPh_3 gave the rhenium(V) S,N-chelated thiosemicarbazide(3−) complexes $[ReX_2(NNCSNHR)(PPh_3)_2]$. On extended reflux for X = Cl the purple imide–hydrazide $[ReCl_2(NH)(NHNH_2)(PPh_3)_2]$ was formed, and a crystal structure determination showed a pseudo-octahedral geometry with *trans* PPh_3 and nitrogen ligands and a significantly bent M–N–N system (145.5°). Further reflux gave the known nitride complex $[Re(N)Cl_2(PPh_3)_2]$ in good yield.

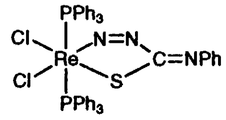
The present level of interest in metal complexes of thiosemicarbazides and thiosemicarbazones stems from the fact that the biological activity of the organic compound is enhanced by co-ordination to a transition metal.[1] There is a wide spectrum of biological activities which are a function of the presence of N–C=S group. These include activity against viruses, protozoa, smallpox and some tumours and they have been suggested as possible pesticides or fungicides. In the vast majority of the known complexes the hydrazide or hydrazone is ligated *via* the thione sulfur and a hydrazinic nitrogen to give a monoanionic five-membered chelate ring. Our interest in these complexes arises from our long-term studies of the reactions of substituted hydrazines with second- and third-row transition metals such as Mo, W, Tc and Re. The product obtained is a sensitive function of the substituents on the hydrazine, and diazenide, dinitrogen, diazene, imide, hydrazide(3−), hydrazide(2−) or hydrazide(1−) complexes can all be prepared.

In earlier work we showed that the aromatic thiohydrazides $RCSNHNH_2$ react with $[MoO_4]^-$ to give complexes of the type $[Mo(HNNCSR)_3]$ in which the thiohydrazide has lost two protons and functions as a highly delocalised dithiolene-type ligand.[2] Aroylhydrazides of the type $RCONHNH_2$ react with $[Re(O)Cl_3(PPh_3)_2]$ to give the chelated complexes $[ReCl_2(NNCOPh)(PPh_3)_2]$ which contain an O,N-chelated aroylhydrazide(3−) ligand.[3] The NNCOPh ligand could be readily converted to co-ordinated dinitrogen and methyl benzoate by reaction with phosphines such as PMe_2Ph in methanol. Analogues of this complex with S in place of O were also prepared by the same route using $RCSNHNH_2$.[4] It was of interest to see if thiosemicarbazides would form analogous chelated derivatives and whether these would undergo reactions to give new NN ligand systems. We report here the sequential formation and characterisation of three complexes from the reaction of $[Re(O)X_3(PPh_3)_2]$ with thiosemicarbazides in the presence of HX.

Results and Discussion

Thiosemicarbazido(3−) *Complexes*.—The rhenium(V) precursors $[Re(O)X_3(PPh_3)_2]$ (X = Cl or Br) react with thiosemicarbazides $RNHCSNHNH_2$ (R = Me or Ph) in 1:1 toluene–methanol under reflux in the presence of aqueous HX for 10 min to give dark green complexes of the type $[ReX_2(NNCSNHR)(PPh_3)_2]$ (X = Cl, R = Ph **1**; X = Br, R = Ph **2**; X = Cl, R = Me **3**). The analytical and spectroscopic data for these complexes and those discussed below appear in the Experimental section. The bromo phenylthiosemicarbazido complex had spectroscopic properties virtually identical to its chloro analogue. All these complexes are air stable in the solid state and in solution, and are non-electrolytes in dichloromethane. It would, in principle, have been possible to have lost all four protons of the thiosemicarbazide ligand to give a chelate ligand with a formal 2− charge, structure **I**, see below. However this would have required the Re to be in the IV oxidation state and therefore paramagnetic, and furthermore clear evidence for the retention of one NH proton comes from the observation of a weak band due to ν(NH) at about 3160 cm^{-1} in the IR spectra and a singlet in the ^1H NMR spectra integrating as 1 H at δ 5.3 (**3**). This resonance disappears on the addition of D_2O and the doublet observed for the methyl group collapses to a singlet (see below). No resonances for the NH protons are observable for the phenyl-substituted complexes **1** and **2** probably as they are obscured by phenyl proton resonances. The observation of ions in the fast atom bombardment (FAB) mass spectra at 945 (**1**) and 884 (**3**) with appropriate isotope distribution corresponding to M^+ and $(M+1)^+$ respectively is also consistent with the above stoichiometry. The appearance of a singlet in the ^{31}P NMR for all the complexes suggests that the P atoms are *trans*.

The exact location of the single proton might be problematic as it could in principle be on any of the three nitrogen atoms as shown in (**a**–**c**). However the observation of a doublet for the methyl group of the methylthiosemicarbazido(3−) complex **3** due to coupling with the NH proton (J_{NH} = 5.2 Hz), confirms that the actual structure is as in **c** with Ph replaced by Me. The appearance of the Me group as a singlet at δ 31.23 in the



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

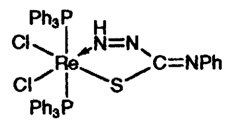
Table 1 Selected bond lengths (Å) and angles (°) for complex **4**

Re(1)–Cl(11)	2.369(2)	Re(1)–N(11)	1.712(8)	Re(3)–N(32)	1.893(6)	Re(2)–P(22)	2.521(2)
Re(2)–Cl(21)	2.373(2)	Re(2)–N(21)	1.705(8)	Re(1)–P(11)	2.542(2)	Re(3)–P(32)	2.538(2)
Re(3)–Cl(31)	2.386(2)	Re(3)–N(31)	1.700(7)	Re(2)–P(21)	2.536(2)	N(12)–N(121)	1.34(2)
Re(1)–Cl(12)	2.428(2)	Re(1)–N(12)	1.894(7)	Re(3)–P(31)	2.528(2)	N(22)–N(221)	1.40(2)
Re(2)–Cl(22)	2.431(2)	Re(2)–N(22)	1.893(6)	Re(1)–P(12)	2.534(2)	N(32)–N(321)	1.41(1)
Re(3)–Cl(32)	2.441(2)						
Cl(11)–Re(1)–Cl(12)	175.2(1)	Cl(11)–Re(1)–N(12)	90.6(2)	Cl(12)–Re(1)–N(12)	84.9(2)	P(12)–Re(1)–N(11)	92.0(2)
Cl(21)–Re(2)–Cl(22)	176.0(1)	Cl(21)–Re(2)–N(22)	90.8(2)	Cl(22)–Re(2)–N(22)	85.2(2)	P(22)–Re(2)–N(21)	88.1(2)
Cl(31)–Re(3)–Cl(32)	173.38(9)	Cl(31)–Re(3)–N(32)	89.3(2)	Cl(32)–Re(3)–N(32)	84.4(2)	P(32)–Re(3)–N(31)	92.3(2)
Cl(11)–Re(1)–P(11)	91.43(8)	Cl(12)–Re(1)–P(11)	87.10(8)	P(11)–Re(1)–P(12)	176.98(8)	P(12)–Re(1)–N(12)	85.1(2)
Cl(21)–Re(2)–P(21)	93.49(8)	Cl(22)–Re(2)–P(21)	86.70(8)	P(21)–Re(2)–P(22)	177.57(7)	P(22)–Re(2)–N(22)	88.4(2)
Cl(31)–Re(3)–P(31)	84.81(7)	Cl(32)–Re(3)–P(31)	96.96(8)	P(31)–Re(3)–P(32)	178.21(7)	P(32)–Re(3)–N(32)	92.0(2)
Cl(11)–Re(1)–P(12)	86.42(8)	Cl(12)–Re(1)–P(12)	94.85(8)	P(11)–Re(1)–N(11)	90.3(2)	N(11)–Re(1)–N(12)	174.0(3)
Cl(21)–Re(2)–P(22)	84.15(8)	Cl(22)–Re(2)–P(22)	95.60(8)	P(21)–Re(2)–N(21)	92.7(2)	N(21)–Re(2)–N(22)	172.7(3)
Cl(31)–Re(3)–P(32)	93.75(7)	Cl(32)–Re(3)–P(32)	84.58(7)	P(31)–Re(3)–N(31)	86.8(2)	N(31)–Re(3)–N(32)	172.7(3)
Cl(11)–Re(1)–N(11)	94.5(3)	Cl(12)–Re(1)–N(11)	90.1(3)	P(11)–Re(1)–N(12)	92.8(2)	Re(1)–N(12)–N(121)	145.4(7)
Cl(21)–Re(2)–N(21)	95.3(2)	Cl(22)–Re(2)–N(21)	88.8(2)	P(21)–Re(2)–N(22)	91.0(2)	Re(2)–N(22)–N(221)	147.6(8)
Cl(31)–Re(3)–N(31)	96.3(2)	Cl(32)–Re(3)–N(31)	90.2(2)	P(31)–Re(3)–N(32)	89.0(2)	Re(3)–N(32)–N(321)	147.6(7)

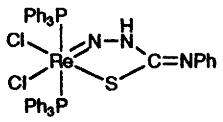
Table 2 Some bond lengths (Å) and angles (°) for imido and hydrazido(1 –) complexes

Complex[a]	M–N	N–N	M–N–N	Ref.
$[ReCl_3(NPh)(PPh_3)_2]$	1.685(11)	—	—	5
$[MoCl_2(NH)O(OPPh_2Et)_2]$	1.70(1)	—	—	6
$[WBr(NH)(Ph_2PCH_2CH_2PPh_2)_2]^+$	1.697(42)	—	—	7
$[ReCl_2(\mathit{NH})(NHNH_2)(PPh_3)_2]$	1.700(7)–1.712(8)	—	—	This work
$[ReBr_2(NNPh)(\mathit{NNHPh})(PPh_3)_2]$	1.992(11)	1.287(15)	131.20(10)	8
$[Mo\{HB(Me_2pz)_3\}(NO)I(NHNMe_2)]$[b]	1.88(3)	1.37(4)	140.3(15)–144(2)	9
$[ReCl_2(NNHCOPh)(\mathit{NHNHCOPh})(PPh_3)_2]$	2.211	1.440	116.1	10
$[ReCl_2(NH)(\mathit{NHNH_2})(PPh_3)_2]$	1.893(6)–1.894(7)	1.34(2)–1.41(1)	145.5(7)–147.6(8)	This work
$[ReCl_2(\mathit{N})(NNPh_2)(PPh_3)_2]$	1.653(5)	—	—	11
$[ReCl_2(N)(\mathit{NNPh_2})(PPh_3)]$	1.837(5)	1.280(6)	142.9(4)	11
$[ReCl_2(\mathit{NH_3})(NNCOPh)(PPh_3)]$	2.16(2)	—	—	11

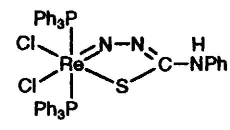
[a] Data refers to the ligand in italics. [b] Me_2pz = 3,5-dimethylpyrazolyl.



a



b



c

^{13}C-{^1H} NMR spectrum indicates that the doublet is due to coupling to the NH proton rather than inequivalence due to restricted rotation about the C–N bond. Additional peaks were observed in the ^1H NMR spectrum at *ca.* 15.5 and 9 of variable integration which do not exchange with D_2O and are not assigned with any certainty. Whatever their origin they do not appear to be directly bound to the metal as there is unambiguous observation of the mass ions in the FAB mass spectrum. The complexes are non-electrolytes which also rules out the presence of NH-containing cations and there is no NMR evidence for the presence of Et groups of NEt_3H^+ cations. Moreover the elemental analysis is consistent with the proposed structure. Attempts to grow crystals suitable for a crystal structure determination have so far been unsuccessful.

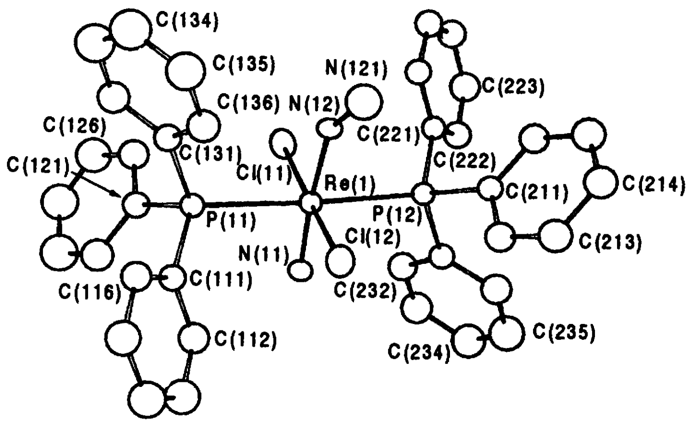


Fig. 1 Molecular structure of $[ReCl_2(NH)(NHNH_2)(PPh_3)_2]$

Imide–Hydrazido(1 –) *Complexes.*—If the reaction time for complex **1** is extended to 25 min, evaporation of the solvent and recrystallisation of the residue gave a purple complex of apparent stoichiometry '$ReCl_2N(N_2)(PPh_3)_2$' **4**. This complex was air stable in the solid state and in solution although sparingly soluble, and the conductivity of solutions in dichloromethane indicates that the complex is a non-electrolyte. The IR spectrum showed two weak bands in the 3100–3300 cm^{-1} region which were assigned to NH bonds, and the ^{31}P NMR showed a weak singlet suggesting that the P atoms are *trans*. The sparing solubility of the complex precluded observation of the NH protons in the ^1H NMR. These data were not sufficient to assign an unequivocal structure for the complex, and accordingly an X-ray diffraction study was undertaken on a suitable crystal grown from dichloromethane–methanol.

Crystal structure of $[ReCl_2(NH)(NHNH_2)(PPh_3)_2]$. A view of the structure appears in Fig. 1 together with the atom labelling scheme. Selected bond lengths and angles are presented in Table 1, atomic coordinates in Table 3 and details of the structure determination in Table 4. The unit cell contains

Table 3 Fractional atomic coordinates for complex **4**

Atom	*x*	*y*	*z*
Re(1)	0.014 53(2)	0.239 86(2)	0.773 44(1)
Re(2)	0.396 39(2)	0.247 15(2)	0.107 88(1)
Re(3)	0.659 99(2)	0.245 16(2)	0.439 92(1)
C(11)	0.008 2(2)	0.109 6(1)	0.735 35(9)
C(12)	0.016 3(2)	0.377 0(1)	0.805 5(1)
C(21)	0.352 1(2)	0.128 5(1)	0.056 16(9)
C(22)	0.441 7(2)	0.373 9(1)	0.155 4(1)
C(31)	0.619 7(2)	0.127 9(1)	0.385 64(8)
C(32)	0.708 1(2)	0.373 0(1)	0.486 51(9)
P(11)	−0.204 8(2)	0.233 6(1)	0.770 95(8)
P(12)	0.232 7(2)	0.243 1(1)	0.771 09(7)
P(21)	0.612 8(2)	0.240 1(1)	0.103 74(7)
P(22)	0.180 1(2)	0.249 9(1)	0.108 85(8)
P(31)	0.442 7(2)	0.244 2(1)	0.442 92(7)
P(32)	0.877 4(2)	0.241 4(1)	0.436 93(7)
N(11)	0.010 1(5)	0.209 0(4)	0.835 0(3)
N(12)	0.029 1(5)	0.283 7(3)	0.708 0(2)
N(21)	0.385 5(5)	0.201 7(4)	0.164 9(3)
N(22)	0.400 9(5)	0.308 7(3)	0.049 0(2)
N(31)	0.650 0(5)	0.198 6(3)	0.496 3(2)
N(32)	0.661 2(4)	0.307 2(3)	0.381 3(2)
N(121)	0.062 9(9)	0.348 7(6)	0.682 4(4)
N(221)	0.387(1)	0.382 2(7)	0.028 3(5)
N(321)	0.647 5(9)	0.381 7(6)	0.361 0(4)
C(111)	−0.258 4(7)	0.299 2(5)	0.820 4(3)
C(112)	−0.218 5(8)	0.297 7(6)	0.870 5(4)
C(113)	−0.254(1)	0.348 5(7)	0.908 3(5)
C(114)	−0.329(1)	0.403 2(9)	0.897 4(6)
C(115)	−0.370 0(9)	0.404 6(7)	0.847 7(5)
C(116)	−0.335 8(8)	0.354 2(5)	0.809 3(4)
C(121)	−0.281 8(7)	0.135 5(5)	0.779 2(4)
C(122)	−0.350(1)	0.119 8(7)	0.822 3(5)
C(123)	−0.331(1)	−0.001 0(9)	0.748 5(6)
C(124)	−0.394(1)	−0.014(1)	0.790 3(7)
C(125)	−0.406(1)	0.044 3(8)	0.828 0(6)
C(126)	−0.271 3(9)	0.074 3(6)	0.742 1(4)
C(131)	−0.259 7(7)	0.267 5(5)	0.711 4(3)
C(132)	−0.344 1(9)	0.221 8(6)	0.681 3(4)
C(133)	−0.383(1)	0.252 4(8)	0.636 3(6)
C(134)	−0.340(1)	0.326 6(8)	0.622 8(6)
C(135)	−0.260(1)	0.372 9(8)	0.652 4(5)
C(136)	−0.2194(9)	0.342 4(6)	0.696 7(4)
C(211)	0.314 4(6)	0.338 6(5)	0.758 4(3)
C(212)	0.300 4(8)	0.404 1(6)	0.791 1(4)
C(213)	0.361 7(9)	0.476 6(7)	0.783 1(4)
C(214)	0.435 3(9)	0.486 2(6)	0.741 1(4)
C(215)	0.451(1)	0.421 4(7)	0.709 5(5)
C(216)	0.390 7(8)	0.347 9(6)	0.717 8(4)
C(221)	0.283 8(6)	0.173 8(4)	0.721 5(3)
C(222)	0.362 4(8)	0.120 1(6)	0.733 5(4)
C(223)	0.401(1)	0.070 9(7)	0.694 8(5)
C(224)	0.365 2(8)	0.075 5(6)	0.645 7(4)
C(225)	0.288 2(8)	0.129 6(5)	0.633 3(4)
C(226)	0.247 0(7)	0.176 7(5)	0.672 1(3)
C(231)	0.291 5(7)	0.211 9(5)	0.831 2(3)
C(232)	0.247 9(8)	0.138 5(6)	0.848 5(4)
C(233)	0.294(1)	0.110 0(7)	0.892 0(5)
C(234)	0.385(1)	0.155 7(8)	0.918 7(6)
C(235)	0.426(1)	0.226 1(8)	0.902 2(6)
C(236)	0.382 5(9)	0.256 0(7)	0.857 4(4)
C(311)	0.666 1(6)	0.178 3(4)	0.051 6(3)
C(312)	0.620 6(8)	0.099 2(5)	0.046 6(4)
C(313)	0.656 5(9)	0.049 7(6)	0.008 3(4)
C(314)	0.745(1)	0.079 7(7)	−0.026 2(5)
C(315)	0.794(1)	0.155 9(7)	−0.018 2(5)
C(316)	0.754 4(8)	0.204 9(6)	0.019 9(4)
C(321)	0.665 8(7)	0.200 3(5)	0.162 4(3)
C(322)	0.633 6(8)	0.233 1(6)	0.209 3(4)
C(323)	0.672(1)	0.204 9(7)	0.254 6(5)
C(324)	0.742(1)	0.143 9(8)	0.253 6(5)
C(325)	0.778(1)	0.114 2(8)	0.207 3(5)
C(326)	0.740 9(9)	0.142 3(6)	0.161 0(4)
C(331)	0.695 7(6)	0.337 0(5)	0.098 6(3)
C(332)	0.778 7(8)	0.367 5(6)	0.134 0(4)
C(333)	0.836 3(9)	0.443 2(7)	0.129 1(5)
C(334)	0.813(1)	0.486 4(7)	0.090 1(5)
C(335)	0.731(1)	0.454 8(8)	0.051 4(5)
C(336)	0.674 1(9)	0.381 2(6)	0.056 7(4)
C(411)	0.123 0(7)	0.310 8(5)	0.160 0(3)
C(412)	0.162 7(8)	0.391 5(6)	0.164 3(4)
C(413)	0.120(1)	0.440 7(7)	0.202 6(5)
C(414)	0.038(1)	0.407 9(8)	0.235 8(5)
C(415)	0.001(1)	0.331 7(7)	0.232 7(5)
C(416)	0.040 9(9)	0.279 7(6)	0.194 2(4)
C(421)	0.123 2(7)	0.284 1(5)	0.049 3(3)
C(422)	0.049 5(8)	0.432 6(5)	0.047 8(4)
C(423)	0.010 3(8)	0.365 4(6)	0.001 2(4)
C(424)	0.040(1)	0.330 8(7)	−0.043 5(5)
C(425)	0.113 4(9)	0.270 4(6)	−0.042 8(4)
C(426)	0.154 6(9)	0.247 7(6)	0.002 7(4)
C(431)	0.107 3(7)	0.149 7(5)	0.114 3(3)
C(432)	0.140 3(8)	0.101 4(6)	0.152 7(4)
C(433)	0.094(1)	0.023 6(7)	0.154 3(5)
C(434)	0.014(1)	−0.008 0(8)	0.117 7(5)
C(435)	−0.022(1)	0.038 5(8)	0.081 0(5)
C(436)	0.022 9(9)	0.117 6(6)	0.078 9(4)
C(511)	0.383 9(7)	0.281 0(5)	0.384 2(3)
C(512)	0.410 8(8)	0.245 7(6)	0.337 5(4)
C(513)	0.372 2(9)	0.272 9(6)	0.292 6(4)
C(514)	0.306 7(9)	0.338 0(6)	0.293 1(4)
C(515)	0.277 7(9)	0.370 3(7)	0.339 3(5)
C(516)	0.315 4(8)	0.343 2(6)	0.385 1(4)
C(521)	0.383 0(6)	0.300 8(5)	0.495 8(3)
C(522)	0.428 4(8)	0.378 8(6)	0.508 4(4)
C(523)	0.384(1)	0.422 2(7)	0.546 8(5)
C(524)	0.244 5(9)	0.313 6(7)	0.462 3(4)
C(525)	0.292(1)	0.388 4(7)	0.575 2(5)
C(526)	0.288 4(8)	0.268 1(5)	0.523 3(4)
C(531)	0.371 5(6)	0.143 2(4)	0.448 5(3)
C(532)	0.404 8(7)	0.098 0(5)	0.487 3(3)
C(533)	0.352 6(8)	0.021 4(6)	0.493 0(4)
C(534)	0.267 8(9)	−0.010 9(7)	0.459 6(5)
C(535)	0.233(1)	0.034 3(7)	0.420 1(5)
C(536)	0.284 1(8)	0.111 2(6)	0.414 8(4)
C(611)	0.935 9(6)	0.181 2(4)	0.385 6(3)
C(612)	1.023 0(7)	0.212 3(5)	0.353 4(3)
C(613)	1.064 6(8)	0.165 1(5)	0.314 8(4)
C(614)	1.022 8(8)	0.085 6(6)	0.308 2(4)
C(615)	0.936 1(8)	0.054 4(5)	0.340 5(4)
C(616)	0.893 0(7)	0.101 2(5)	0.378 5(3)
C(621)	0.927 3(6)	0.201 1(5)	0.496 4(3)
C(622)	0.887 2(7)	0.230 4(5)	0.543 2(3)
C(623)	0.920 1(8)	0.200 7(5)	0.588 2(4)
C(624)	0.993 5(9)	0.139 1(6)	0.587 5(4)
C(625)	1.031 6(8)	0.111 5(5)	0.541 4(4)
C(626)	1.000 3(7)	0.141 6(5)	0.495 7(3)
C(631)	0.957 8(7)	0.339 9(5)	0.433 5(3)
C(632)	1.038 6(8)	0.370 5(6)	0.469 9(4)
C(633)	1.095(1)	0.446 4(7)	0.467 4(5)
C(634)	1.068(1)	0.492 6(7)	0.428.3(5)
C(635)	0.990(1)	0.462 0(7)	0.390 5(5)
C(636)	0.933 8(8)	0.386 3(6)	0.392 9(4)

three independent molecules which have virtually identical structures, which are here discussed together. The geometry about Re is distorted octahedral with the triphenylphosphine ligands *trans* as suggested from the ^{31}P NMR spectrum. The Re–P and Re–Cl distances (2.521–2.542 and 2.369–2.441 Å respectively) are unremarkable.

There is a more complex situation with respect to the two nitrogen ligands. The diamagnetism of the complex shows that

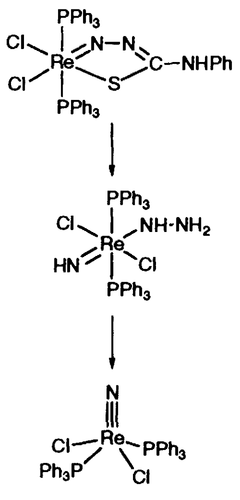
Table 4 Summary of crystal data, data collection and structure refinement for complex **4**

Empirical formula	$C_{36}H_{34}Cl_2N_3P_2Re$
Colour, habit	Purple plate
M	826
Crystal system	Triclinic
Space group	$P\bar{1}$
Crystal size/mm	0.15 × 0.30 × 0.60
a/Å	11.639(1)
b/Å	16.920(1)
c/Å	26.076(3)
α/°	92.64(1)
β/°	90.42(1)
γ/°	96.202(9)
U/Å^{-3}	5099(1)
Z	6
D_c/g cm^{-3}	1.621
F(000)	2472
Diffractometer	Enraf-Nonius CAD4
Radiation	Mo-Kα (λ = 0.071 073 Å)
T/K	291
Collection method	ω–2θ
θ range/°	1.5–25
Index ranges	h −13 to 13, k −20 to 20, l 0–30
Reflections collected	18 317
Independent reflections	17 886
Reflections observed [$I > 3\sigma(I)$]	12 898
Program used	MOLEN[12]
Solution method	Patterson
Weighting scheme	w = 1.0
R, R'	0.039, 0.044
S	4.65
$(\Delta/\sigma)_{max}$	0.10
Maximum, minimum $\Delta\rho$/e Å^{-3}	1.07, −0.41

the formal charge on both of these ligands together must be 1−, 3− or 5− and possible combinations include ≡N and NH_2NH_2, ≡N and NNH_2, =NH and $NHNH_2$, =NH and N=NH, NH_2 and =NNH_2, NH_3 and N=NH. Some pertinent literature X-ray data for other complexes containing these types of ligand appear in Table 2.

To deal with the N(11) ligand first, the Re–N(11) and related distances [1.700(7)–1.712(8) Å] are significantly longer than the normal Re–N nitride bond length of about 1.6–1.65 Å.[13] The NH_2 and NH_3 possibilities are ruled out on the basis that their metal–nitrogen bond lengths [1.85–1.90 for amide and 2.16(2) Å for NH_3, see Table 2] are generally significantly longer than the Re–N(11) distances found here. Significantly there are also no reported examples of nitride complexes where there is a multiply bonded ligand *trans* to nitride. The N^{3-} ligand is an exceptionally strong π-donor ligand and the disposition of a multiply bonded ligand *trans* is unlikely due to competition for metal orbitals. Moreover, the Re–N(11) distance compares closely with the range found for M=NH complexes in the literature [1.693(42)–1.70(1) Å, see Table 2]. The observed structural data are therefore most consistent with the presence of an imide (NH) ligand.

The NH/N=NH combination would appear to be ruled out on the basis that the N–N distance is too long for a species with substantial N–N π bonding. The N–N distance in aryldiazenido complexes is generally of the order of 1.25 Å.[14] We conclude that the NH/$NHNH_2$ structure fits best with the observed structural data. A few $NHNH_2$ complexes have been reported[15–18] and all of these have been η^2 bonded to the metal *via* both nitrogens. In this instance the bulk of the PPh_3 ligands presumably prevents the hydrazide(1−) ligand binding side-on to the metal. There is a limited number of monodentate hydrazido(1−) complexes for which the structures are known[4,10] and the geometry of the N–N system is highly dependent on the hydrazine substituent and the metal involved.



Scheme 1

The N–N bond distances found here are within the range found for these hydrazide(1−) ligands as are the M–N–N angles (145.4–147.6°).

It is of interest to compare this structure with that of $[ReCl_2(NH_3)(NNCOPh)(PPh_3)_2]$ and $[ReCl_2(N)(NNPh_2)(PPh_3)]$[11] (see Table 2). In the ammonia complex the M–NH_3 distance of 2.16(2) Å certainly argues against the presence of ammonia in complex **4**, and the two nitrogen ligands are *cis* as opposed to *trans*. The co-ordination number of five in the nitride–hydrazide(2−) complex makes detailed comparison difficult, and the bulky phenylhydrazide substituents have undoubtedly had a significant effect on the structure.

Formation of $[Re(N)Cl_2(PPh_3)_2]$.—If the reaction mixture is heated under reflux for 3 h or longer the well known nitrido complex $[Re(N)Cl_2(PPh_3)_2]$ can be isolated in good yield. The overall reaction scheme for the formation of the nitride from the chelated thiosemicarbazido complex is summarised in Scheme 1. The mechanism involved is complex, as the reaction mixture contains HCl and excess thiosemicarbazide. Both of these appear necessary, the thiosemicarbazide to introduce the third nitrogen and the acid to promote the cleavage of the N–N bond. It was observed in the original preparation of the nitride complex from hydrazine and $[Re(O)Cl_3(PPh_3)_2]$ that acid was required to produce the nitride complex. This is also illustrated by the reaction of phenylhydrazine with the same precursor where without HCl the diazenide $[ReCl(NNPh)_2(PPh_3)_2]$ is formed in high yield,[7] but in the presence of acid again the nitride is the predominant product. Neither the chelated complex nor the imide–hydrazide degrade to the nitride when heated alone in toluene–ethanol mixtures. We have looked for the organic by-products of the reaction using HPLC and GLC, but have been unable to identify any with certainty, and the mechanism of loss of the PhNHCS group remains uncertain.

Experimental

All manipulations were carried out under an atmosphere of dinitrogen using conventional Schlenk-type apparatus. Elemental analyses were performed by Medac Ltd., University of Brunel using a CEC 240Xa or Carlo Elba 1106 instrument. Fast atom bombardment mass spectra were carried out using 3-nitrobenzyl alcohol as the matrix material. Infrared spectra were recorded in the range 200–4000 cm^{-1} as Nujol mulls on KBr plates on a Perkin-Elmer 1330 spectrophotometer, ^{1}H and ^{13}C NMR spectra were measured using a EX270 (270 MHz) NMR spectrometer in $CDCl_3$ solutions. The complexes $[Re(O)Cl_3(PPh_3)_2]$ and $[Re(O)Br_3(PPh_3)_2]$ were prepared by a slight modification of the literature method,[20] using acetone as the reaction solvent.

Dichloro[*4-phenylthiosemicarbazido*(3 −)-S,N]*bis*(*triphenylphosphine*)*ruthenium*(V) **1**.—The compounds $[Re(O)Cl_3(PPh_3)_2]$ (0.25 g, 0.26 mmol), PPh_3 (0.25 g), 4-phenylthiosemicarbazide (0.05 g, 0.3 mmol) and concentrated HCl (5 cm^3) were heated under reflux for 10 min in 1 : 1 toluene–methanol (50 cm^3). The resulting dark green precipitate was filtered off in air and washed with diethyl ether (Found: C, 54.3; H, 3.9; N, 4.5. Calc. for $C_{43}H_{36}Cl_2N_3P_2ReS$: C, 54.6; H, 3.8; N, 4.4%). IR (cm^{-1}) 3140 ν(N–H) 1600m, ν(N=N). NMR ($CDCl_3$): ^{1}H, δ 7.3–7.7 (m, phenyl protons); ^{31}P, δ −5.1 (s). Mass spectrum (FAB): *m*/*z* 945 (M^+), appropriate isotope distribution.

Dibromo[*4-phenylthiosemicarbazido*(3 −)-S,N]*bis*(*triphenylphosphine*)*rhenium*(V) **2**.—Prepared in an analogous manner to **1** using $[Re(O)Br_3(PPh_3)_2]$ (Found: C, 49.6; H, 4.4; N, 3.9. Calc. for $C_{43}H_{36}Br_2N_3P_2ReS$: C, 50.0; H, 3.5; N, 4.1%). IR and ^{1}H NMR spectra as for Cl complex. ^{31}P NMR: δ −5.7 (s).

Dichloro[*4-methylthiosemicarbazido*(3 −)-S,N]*bis*(*triphenylphosphine*)*rhenium*(V) **3**.—Prepared as for complex **1** using 4-methylthiosemicarbazide (Found: C, 51.9; H, 3.9; N, 4.4. Calc. for $C_{38}H_{34}Cl_2N_3P_2ReS$: C, 51.6; H, 3.9; N, 4.8%). IR (cm^{-1} 3160w ν(N–H), 1750m ν(N=N). NMR: ^{1}H, δ 7.3–7.9 (m, 30 H, phenyl protons), 2.6 (d, 3 H, $NHCH_3$), 5.3 (s, 1 H, NH); ^{31}P, δ −3.8 (s). Mass spectrum (FAB): *m*/*z* 884 (M^+ + 1), with appropriate isotope distribution.

Dichloro[*hydrazido*(1 −)](*imido*)*bis*(*triphenylphosphine*)*rhenium*(V) **4**.—The reaction mixture as for complex **1** above was heated under reflux for a total of 30 min and the solvent removed *in vacuo*. The residue was recrystallised from dichloromethane–methanol to give purple crystals of **4** (0.16 g, 64%) (Found: C, 52.3; H, 4.1; Cl, 8.9; N, 5.3. Calc. for $C_{36}H_{34}Cl_2N_3P_2Re$: C, 52.2; H, 4.1; Cl, 8.5; N, 5.1%). IR (cm^{-1}) 3125w (br), 3300w (br) ν(N–H). ^{31}P NMR: δ −7.2 (s). Mass spectrum (FAB): *m*/*z* 828 (M^+ + 1) with appropriate isotope distribution.

Dichloro(*nitrido*)*bis*(*triphenylphosphine*)*rhenium*(V).—The reaction mixture as for complex **1** was heated under reflux for at least 3 h and the volume of solvent reduced to half *in vacuo*. The nitrido complex was filtered off as a pink-orange air-stable solid which had the same IR and ^{31}P NMR spectrum as an authentic sample prepared by the literature route.[11]

Crystal Structure Determination for $[ReCl_2(NH)(NHNH_2)(PPh_3)_2]$ **4**.—The details of the structure determination are given in Table 4.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

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