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FULL PAPER

Synthesis, characterization, properties and structures of rhenium-(II), -(III), and -(V) complexes containing amino acids conjugated with a 2-aminothiazole ligand

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The one-step reaction of $KReO_4$ with benzoylhydrazine in the presence of concentrated HCl and PPh_3 afforded $[Re^V(NNC(Ph)O)(PPh_3)_2Cl_2]$ **1** which was converted with carbon monoxide into the dinitrogen Re(I) complex $[ReN_2(CO)_2(PPh_3)_2Cl]$ **2** in good yield. A new class of ligands, of general formula HL^n ($n = 1$–5), was obtained by conjugation of N-protected amino acids and benzoic acid with 2-aminothiazole. Complex **2** reacted with HL^n to give neutral Re(II) chelate complexes $[Re(L^n)(CO)(PPh_3)_2Cl]$ **5**–**9** ($n = 1$–5), by substitution of N_2 and CO groups. The molecular structure of complex **9** was determined by X-ray diffraction. When reactions between $[Re(NNC(Ph)O)(PPh_3)_2Cl_2]$ **1** and HL^n ($n = 2, 5$) were carried out in different stoichiometric ratios, neutral mono- and di-substituted Re(III) organodiazenido complexes $[Re(NNCOPh)(L^{2,5})(PPh_3)_2Cl]$ **10**, **11** and $[Re(NNCOPh)(L^5)_2(PPh_3)]$ **12** were obtained. In these complexes the organodiazenido Re–N–N moiety adopts a linear conformation, as has been authenticated by X-ray diffraction analysis for **11** and **12**. Treatment of Re(I) dinitrogen precursors $[ReN_2(P)_4Cl]$ ($P = PMe_2Ph$, **3** and $PMePh_2$, **4**) with ligands resulted in interesting dinuclear oxo-(μ-oxo)-Re(V) species $[Re_2(O)_3(L^n)_2(P)_2]$ ($P = PMe_2Ph$, $n = 1$, **13**; $n = 2$, **14**; $n = 4$, **15**. $P = PMePh_2$, $n = 2$, **16**). Suitable crystals for an X-ray analysis have been obtained for complex **14**. The structure represents one of the few cases where, for steric reasons, the Re–O–Re bridging unit is not linear but rather bent. All the compounds have been characterized by elemental analyses, IR and NMR spectroscopy. The Re(II) complexes **5**–**7** and **9** were further characterized by electrochemical measurements.

Introduction

Research in the chemistry of technetium and rhenium complexes arises from the use of diagnostic ^{99m}Tc and therapeutic $^{186/188}Re$ radiopharmaceuticals in nuclear medicine. In particular, the success of the $^{186}Re(Sn)$HEDP (HEDP = hydroxyethylenediphosphonic acid) radiopharmaceutical as a palliative of bone pain,[1] has reawakened interest in the co-ordination chemistry of rhenium in order to develop new $^{186/188}Re$ radiopharmaceuticals having specificity to be used for the treatment of cancer.

A recent approach to the development of site specific radiopharmaceutical and/or radioimaging agents is to derivatize a chelate, which binds a radionuclide, with a biomolecule (bifunctional chelating agent, BFCA approach) whose purpose is to carry the radionuclide to a specific site. There is considerable interest in the design of new ligands; in particular derivatized amino acids and peptides have attracted attention over the past fifteen years and new radiopharmaceuticals have been applied in nuclear medicine.[2]

Selection of a BFCA is largely determined by the nature and oxidation state of the metal and its co-ordination chemistry will determine the geometry and stability of the final complex. Many stable complexes of Re(V) and Tc(V) have been reported because this high oxidation state is easily accessible by reduction of the $[MO_4]^-$ anions. Some of these complexes display remarkable bioactivity themselves,[3] other are used as intermediates in the preparation of lower oxidation state compounds.

Although analogous technetium and rhenium complexes exhibit similar physical properties, chemical differences can result in their biological behavior due to redox potentials of the central metal. It is well known that rhenium complexes are more difficult to reduce than the corresponding technetium compounds. As an example, we can mention a comparative study *in vivo* between two cations, $[^{99m}Tc(DMPE)_2Cl_2]^+$ and $[^{186}Re(DMPE)_2Cl_2]^+$ [DMPE = 1,2-bis(dimethylphosphino)ethane] for which it was shown that the reduction occurs only for the technetium complex, not for the rhenium analogue.[4]

In contrast, in the +1 oxidation state the similarity in chemical behavior between the two elements is particularly strict. Useful synthetic procedures have been reported to obtain precursors of rhenium and technetium in lower oxidation states and emphasis has been placed on Re(I) and Tc(I) chemistry.[5] The value of these compounds has been increased recently since the discovery of a new safe and easy synthetic route to the complex $[M(H_2O)_3(CO)_3]^+$ (M = Re, Tc) which avoids the use of dangerous CO and therefore allows the preparation of $^{99m}Tc(I)$ compounds for radiopharmaceutical applications.[6] The chemistry of this complex is of great interest due to the high stability of the *fac*-$[M(CO)_3]^+$ core and lability of aquo ligands which can be easily substituted by a variety of appropriate ligands.[6b] An alternative idea has been proposed by Katzenellenbogen who has bound bioactive molecules to the cyclopentadienyl

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ring obtaining analogues of the organometallic compound $[(Cp)M(CO)_3]$.[7] It is worth noticing that organometallic compounds of Re(I) could provide valuable alternatives as radiopharmaceutical species.[8]

An interesting exception is represented by the synthetic access to low oxidation states of rhenium reported by Chatt[9] based on the use of the chelate Re(V) complex $[Re(NNC(Ph)O)(PPh_3)_2Cl_2]$ **1** as a versatile precursor. It reacts with neutral monodentate ligands L such as CH_3CN, CO and tertiary phosphines, to give organodiazenido complexes, of general formula $[Re(NNCOPh)(L)(PPh_3)_2Cl_2]$, through displacement of the weakly coordinated carbonyl oxygen atom of the chelate ring Re–NNC(Ph)O–.[9] Moreover, complex **1**, as well as organodiazenido derivatives, is a good synthon to form Re(I) dinitrogen complexes $[ReN_2(L)_2(PPh_3)_2Cl]$ (L = CO, tertiary phosphines).[10] A series of Re(I) and Re(II) complexes with nitrogen donor ligands have been prepared giving interesting compounds for a study of low-valent rhenium co-ordination chemistry.[11a–c] Thus, the methodology developed by Chatt[9,10] and others[11] seems to represent an alternative and facile synthetic approach to obtain new rhenium complexes in low oxidation states.

We previously reported on reactions of the Re(I) and Tc(I) carbonyl complexes $[M(CO)_3(PPh_3)_2Cl]$ with 2-aminothiazole and its derivatives and the chemistry of the corresponding complexes has been extensively studied.[12] More recently we described the synthesis and characterization of a Re(I) carbonyl complex containing a bile acid functionalized with 2-aminothiazole ligand as an example of a BFCA.[13]

Along these lines, we report here the synthesis of a new class of ligands obtained from conjugation of amino acids with 2-aminothiazole, which is a good moiety for the formation of rhenium complexes in low oxidation states. Afterwards, we have investigated the reactivity of these ligands toward the dinitrogen precursors of Re(I), $[ReN_2(CO)_2(PPh_3)_2Cl]$ **2** and $[ReN_2(P)_4Cl]$ (P = PMe_2Ph, **3**; $PMePh_2$, **4**), and the chelate Re(V) complex $[Re(NNC(Ph)O)(PPh_3)_2Cl_2]$ **1**.

Complexes of Re(II), Re(III) and Re(V) were obtained and authenticated by X-ray crystallography. We also report the electrochemistry for rhenium(II) complexes. Furthermore, a modified one-step procedure for the synthesis of $[ReN_2(CO)_2(PPh_3)_2Cl]$ **2** is also presented.

Results and discussion

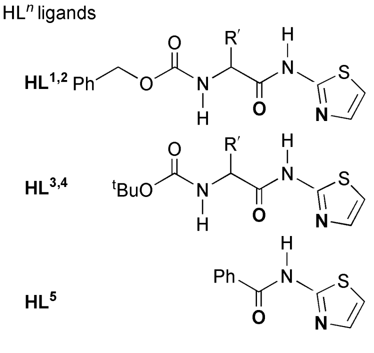
Synthesis of HL$^{1-5}$ ligands

This class of ligands was synthesized by coupling reactions between the amino group of 2-aminothiazole with the carboxylic group of N-protected amino acids (L configuration) and benzoic acid or its corresponding benzoyl chloride, following a general procedure previously reported by us.[14] These ligands are stable in the solid state for several months, and were completely characterized on the basis of their elemental analysis, melting point, IR and ^{1}H NMR spectra (see Experimental section).

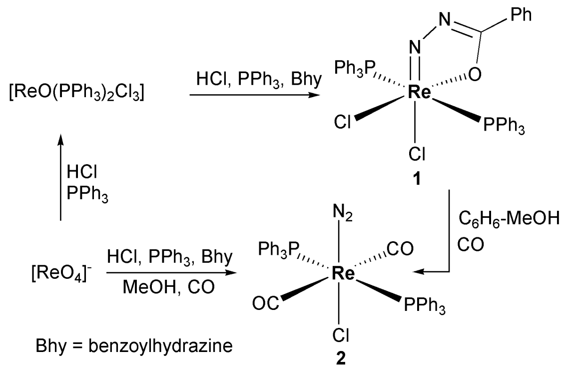
Preparation of $[ReN_2(CO)_2(PPh_3)_2Cl]$ 2

The original preparation of the complex $[ReN_2(CO)_2(PPh_3)_2Cl]$ **2** described by Chatt and co-workers[10] is performed by the treatment of the benzoylhydrazido Re(V) complex $[Re(NNC(Ph)O)(PPh_3)_2Cl_2]$ **1** with a stream of carbon monoxide in a boiling methanol–benzene mixture. The starting material **1** is prepared from the oxo-complex $[ReO(PPh_3)_2Cl_3]$.[9]

In order to provide a more convenient route to synthesize complexes **1** and **2**, we propose a one-pot reaction, starting from $[ReO_4]^-$ (see Scheme 1). The perrhenate salt in CH_2Cl_2 in the presence of an excess of PPh_3, aqueous HCl, and benzoylhydrazine, promptly gives $[Re(NNC(Ph)O)(PPh_3)_2Cl_2]$ **1**; the latter, in MeOH, can be converted into $[ReN_2(CO)_2(PPh_3)_2Cl]$ **2** in good yield when CO is bubbled for 45 minutes into the reaction mixture.



***n* = 1** R′ = CH_3 ; [1-(Thiazol-2-ylcarbamoyl)-ethyl]-carbamic acid benzyl ester
***n* = 2** R′ = CH_2Ph ; [2-Phenyl-1-(thiazol-2-ylcarbamoyl)-ethyl]-carbamic acid benzyl ester
***n* = 3** R′ = CH_3 ; [1-(Thiazol-2-ylcarbamoyl)-ethyl]-carbamic acid *tert*-butyl ester
***n* = 4** R′ = CH_2Ph ; [2-Phenyl-1-(thiazol-2-ylcarbamoyl)-ethyl]-carbamic acid *tert*-butyl ester
***n* = 5** N-Thiazol-2-yl-benzamide

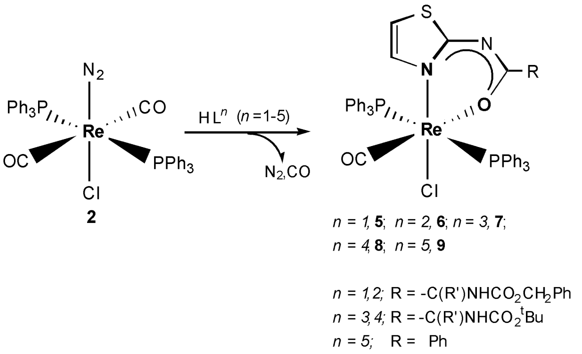


Bhy = benzoylhydrazine

Scheme 1

Preparation and properties of Re(II) complexes $[Re(L^n)(PPh_3)_2(CO)Cl]$ 5–9 (n = 1–5)

Treatment of the dinitrogen complex **2** with the appropriate ligands, in the presence of a base to facilitate their deprotonation, results in the formation of red Re(II) complexes $[Re(L^n)(CO)(PPh_3)_2Cl]$ **5**–**9** (n = 1–5) in good yield (Scheme 2).



n = 1, **5**; n = 2, **6**; n = 3, **7**; n = 4, **8**; n = 5, **9**

n = 1,2; R = -C(R′)NHCO$_2$CH$_2$Ph
n = 3,4; R = -C(R′)NHCO$_2$^{t}Bu
n = 5; R = Ph

Scheme 2

The IR spectra confirm the loss of the N_2 moiety[10,11a,c,d] and exhibit a strong band at around 1830–1845 cm^{-1} assigned to ν(C≡O) vibration; another absorption in the range 1500–1530 cm^{-1} is typical for a co-ordinated CO amidic group.

The very broad signals observed in the ^{1}H NMR spectra combined with the absence of resonances in the $^{31}P\{^1H\}$NMR spectra seems to suggest the formation of paramagnetic derivatives. In agreement with our expectations, the solid-state magnetic moment determined for complexes **5** and **9** was 1.7 μ_B, which supports a Re(II) species. As reported in the literature, the

d^5 low spin electronic configuration is the most probable for Re(II) and usually magnetic moment values have been found in the range 1.5–2.0 μ_B at room temperature for mono- and bi-nuclear complexes.[15] Moreover, an EPR spectrum of **5** collected at 90 K confirmed the presence of an unpaired electron on the metal. The spectrum consists of six lines which are clearly due to the $I = 5/2$ nucleous of rhenium and it is characterized by a g value of 2.11 and a line width of 380 G.

In order to contribute to the understanding of the real nature of complexes **5**–**7** and **9**, we investigated their electrochemical behavior and found it to be similar for all these derivatives. In particular, the redox profile is characterized by the presence of two reversible oxidation processes due to the Re(III/II) and Re(II/I) couples, in the range of +(0.580–0.650) V and −(0.700–0.777) V, respectively (see Experimental section).

UV–Vis spectra of **5** and **9** in CH_2Cl_2 solution were also recorded. These complexes show intense absorptions at 450 and 500 nm ($\varepsilon > 2000$), respectively, assigned to charge-transfer bands rather than d–d transitions.

On the basis of the spectroscopic measurements together with analytical data, we may consider these derivatives as Re(II) neutral complexes $[Re(L^n)(CO)(PPh_3)_2Cl]$ (n = 1–5) where a molecule of deprotonated ligand replaces a carbonyl group and the N_2 molecule in the starting complex **2**. This supposed formulation was unambiguously supported by X-ray crystallographic analysis of the complex $[Re(L^5)(CO)(PPh_3)_2Cl]$ **9**. An ORTEP drawing is shown in Fig. 1 and selected bond distances and angles are reported in Table 1.

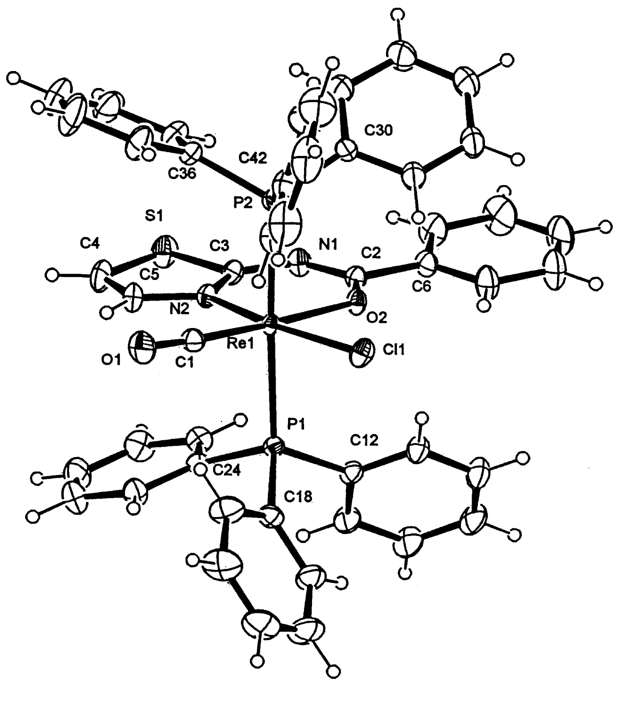


Fig. 1 An ORTEP view of complex **9** showing thermal ellipsoids at 30% probability.

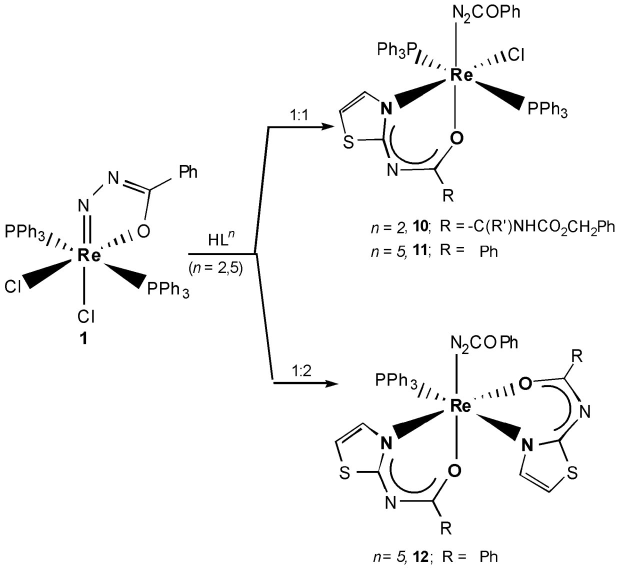
The more usually encountered mononuclear Re(II) complexes contain only halide and phosphine ligands[15b,16] although compounds containing different ligands have been reported and structurally characterized,[17] the chemistry of rhenium in this rather uncommon oxidation state is still relatively unknown. The complexes here reported are examples of stable mononuclear Re(II) species which contain a monoanionic bidentate ligand. The formation of Re(II) complexes was not completely unexpected since a few examples have already been reported.[11b] Nevertheless, it is possible to notice some substantial differences compared to our results. In fact, the Re(II) complexes previously reported in the literature were obtained from the Re(V) precursor **1** and authors have suggested formation of an Re(I) intermediate species which is subsequently oxidized to the final Re(II) product by protic solvent and/or by rhenium species in higher oxidation states. In contrast, our reactions were carried out starting from the Re(I) dinitrogen complex **2** in aprotic solvent (benzene) giving Re(II) as the only observed oxidation state. Control experiments have shown that the result of this process is independent of the presence of both oxygen and water. Therefore, we may presume that **2** undergoes a metal-to-ligand electron transfer to give CO, N_2 and organic by-product.

Table 1 Selected bond distances (Å) and angles (°) for compound **9**

Re1–Cl1	2.3891(7)	O2–C2	1.265(3)
Re1–P1	2.4799(7)	N1–C2	1.328(4)
Re1–P2	2.4682(7)	N1–C3	1.343(4)
Re1–O2	2.132(2)	N2–C3	1.346(4)
Re1–N2	2.087(2)	O1–C2	1.172(4)
Re1–C1	1.857(3)		
Cl1–Re1–P1	88.75(3)	P2–Re1–C1	89.3(1)
Cl1–Re1–P2	90.56(3)	O2–Re1–N2	84.31(8)
Cl1–Re1–O2	84.84(6)	O2–Re1–C1	177.0(1)
Cl1–Re1–N2	169.13(7)	N2–Re1–C1	93.1(1)
Cl1–Re1–C1	97.8(1)	Re1–O2–C2	130.1(2)
P1–Re1–P2	177.43(2)	Re1–N2–C3	124.082)
P1–Re1–O2	88.34(6)	C2–N1–C3	122.3(2)
P1–Re1–N2	90.25(7)	Re1–C1–O1	176.8(3)
P1–Re1–C1	93.2(1)	O2–C2–N1	127.2(2)
P2–Re1–O2	89.13(6)	N1–C3–N2	132.0(2)
P2–Re1–N2	89.96(7)		

Reactions of $[Re(NNC(Ph)O)(PPh_3)_2Cl_2]$ 1 and formation of organodiazenido complexes of Re(III) 10, 11 and 12

We have also investigated alternative pathways to form Re(I) or Re(II) dinitrogen complexes with HL^n (n = 2, 5). Reactions of complex **1** in benzene–methanol with the ligands in stoichiometric ratios give neutral monosubstituted Re(III)-organodiazenido $[Re(NNCOPh)(L^{2,5})(PPh_3)_2Cl]$ **10** and **11** complexes, while with two equivalents of HL^5 the disubstituted $[Re(NNCOPh)(L^5)_2(PPh_3)]$ **12**, is collected (Scheme 3). Further reduction from Re(III) to lower states was not observed even in protic solvents, which we expected to assist the process!



Scheme 3

The infrared spectra of these compounds show a strong band at around 1240 cm^{-1} associated with a vibration of the benzoyl group; absorptions in the range 1504–1510 cm^{-1} and at 1635 cm^{-1} are assigned to $\nu(N{=}N)$ and $\nu(C{=}O)$ of the organodiazenido moiety, Re–NNC(O)Ph, respectively.[9,11c] An additional

Table 2 Selected bond distances (Å) and angles (°) for compound **11**

Re1–Cl1	2.429(2)	O2–C11	1.218(8)
Re1–P1	2.482(2)	N1–C3	1.330(8)
Re1–P2	2.467(2)	N2–C3	1.358(8)
Re1–O1	2.045(4)	N2–C4	1.305(7)
Re1–N1	2.116(5)	N3–N4	1.284(7)
Re1–N3	1.744(5)	N4–C11	1.374(8)
O1–C4	1.303(7)		
Cl1–Re1–P1	88.64(6)	P2–Re1–N3	85.6(1)
Cl1–Re1–P2	90.41(6)	O1–Re1–N1	82.0(2)
Cl1–Re1–O1	82.8(1)	O1–Re1–N3	175.6(2)
Cl1–Re1–N1	164.7(1)	N1–Re1–N3	95.5(2)
Cl1–Re1–N3	99.8(2)	Re1–O1–C4	133.4(4)
P1–Re1–P2	179.0(1)	Re1–N1–C3	124.6(4)
P1–Re1–O1	89.2(1)	C3–N2–C4	121.0(6)
P1–Re1–N1	90.1(1)	Re1–N3–N4	170.1(5)
P1–Re1–N3	94.3(1)	N3–N4–C11	119.6(5)
P2–Re1–O1	90.9(1)	N1–C3–N2	131.2(5)
P2–Re1–N1	90.9(1)	O1–C4–N2	125.4(6)

band at 1722 cm^{-1} in the spectrum of **10** is attributed to ν(C=O)$_{\text{carbam.}}$. The ^{1}H NMR spectra consist of two broad singlets assigned to –CHN and –CHS thiazole protons; the position of these signals is upfield shifted in comparison with those of HL^n indicative of a decreased aromaticity of the thiazole upon co-ordination.[12e,f] A singlet at δ 4.0 observed in the ^{31}P{^{1}H}-NMR spectra of **10** and **11** reveals that the two phosphinic groups are equivalent and in *trans* position to one another; in complex **12** the phosphorus signal resonates at lower field (δ 11.3). Magnetic moment measurements are consistent with the diamagnetic nature of these compounds. It is known that complex **1** reacts with neutral ligands such as CH_3CN, PF_3, py (L), dipy and terpy (LL) to form diamagnetic organodiazenido complexes of the type [Re(NNCOPh)(L)$(PPh_3)_2Cl_2$] or [Re(NNCOPh)(LL)$(PPh_3)Cl_2$].[9,11c] The monodentate organodiazenido ligand –NNAr may exhibit linear, singly bent and double bent conformations and this affects the assignment of the oxidation state of the central metal ion.[18] The crystal structures of **11** and **12** show a singly bent diazenido moiety and they must be considered as Re(III) derivatives according to the assignment proposed by Chatt *et al.*[9,11c] and more recently, also on the basis of X-ray analyses of some rhenium and technetium organodiazenido complexes.[19] The diamagnetic properties of all these Re(III) species may be attributed to a distortion of octahedral symmetry resulting from the organodiazenido ligand.[9,19] Complexes **11** and **12** possess an octahedral geometry with the oxygen atom of the ligand *trans* to the –N_2COPh group. The short Re–N–N bond distances together with the Re–N–N bond angle suggest significant Re–N multiple bonding and a linear geometry for the Re–NN fragment. A selected list of bond distances and angles is given in Tables 2 and 3 and ORTEP views of **11** and **12** are shown in Figs. 2 and 3, respectively.

Oxidation of Re(I) complexes [ReN$_2$(P)$_4$Cl] (P = PMe$_2$Ph, PMePh$_2$) to oxo-(μ-oxo)-Re(V) dimers [Re$_2$(O)$_3$(L^n)$_2$(P)$_2$] (P = PMe$_2$Ph, *n* = 1, 13; *n* = 2, 14; *n* = 4, 15. P = PMePh$_2$, *n* = 2, 16)

The ligands used in the present section are HL^n (*n* = 1, 2, 4). Wishing to obtain Re(I) dinitrogen complexes, the two precursors [ReN$_2$(P)$_4$Cl] (P = PMe$_2$Ph, **3**; PMePh$_2$, **4**) have been combined with these ligands (Scheme 4). Reactions were carried out in boiling benzene, in air and in the presence of NEt$_3$ as deprotonating agent. Complex **3** reacts very slowly with HL^n (*n* = 1, 2, 4) and after 30 h a violet solid could be collected. In the same reaction conditions **4** reacts with HL^2 to give the corresponding violet compound after 6 h. This notable difference in reactivity may be ascribed to the steric hindrance of the phosphines (PMePh$_2$ > PMe$_2$Ph) affecting the substitution rate. The reaction of **3** with HL^5 afforded the Re(III) complex [ReCl$_3$(PMe$_2$Ph)$_3$], also collected when the reaction was carried out in anhydrous solvents and under a nitrogen stream, as well as in the absence of base.

Table 3 Selected bond distances (Å) and angles (°) for compound **12**

Re1–P1	2.406(3)	N1–C3	1.348(16)
Re1–O1	2.021(8)	N2–C3	1.397(12)
Re1–O2	2.040(7)	N2–C4	1.360(14)
Re1–N1	2.087(9)	N3–C13	1.313(13)
Re1–N3	2.134(8)	N4–C13	1.372(12)
Re1–N5	1.753(8)	N4–C14	1.314(12)
O1–C4	1.271(14)	N5–N6	1.279(12)
O2–C14	1.280(12)	N6–C21	1.485(19)
O3–C21	1.200(15)		
P1–Re1–O1	92.4(2)	N3–Re1–N5	97.7(3)
P1–Re1–O2	91.3(2)	Re1–O1–C4	136.3(8)
P1–Re1–N1	93.2(3)	Re1–O2–C14	129.7(6)
P1–Re1–N3	175.4(2)	Re1–N1–C3	123.6(7)
P1–Re1–N5	86.3(3)	C3–N2–C4	121.7(9)
O1–Re1–O2	83.5(3)	Re1–N3–C13	121.9(6)
O1–Re1–N1	84.3(3)	C13–N4–C14	122.3(8)
O1–Re1–N3	83.8(3)	Re1–N5–N6	160.5(8)
O1–Re1–N5	174.8(3)	N5–N6–C21	119
O2–Re1–N1	167.2(3)	N1–C3–N2	131
O2–Re1–N3	85.8(3)	O1–C4–N2	123
O2–Re1–N5	101.6(3)	N3–C13–N4	131.2(9)
N1–Re1–N3	89.0(3)	O2–C14–N4	128.2(9)
N1–Re1–N5	90.7(3)		

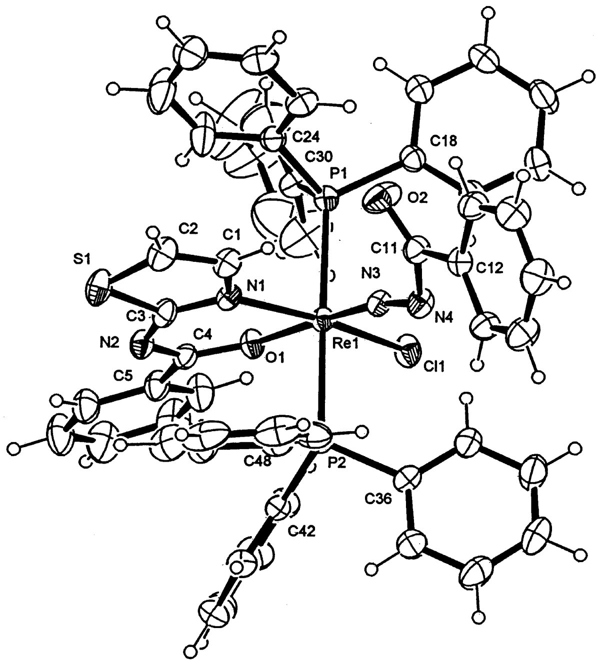


Fig. 2 An ORTEP view of complex **11** showing thermal ellipsoids at 30% probability.

Ligands HL^n are potentially capable of binding through sulfur or nitrogen atoms of thiazole ring and amidic or carbamic groups. FTIR spectra of **13**–**16** show two stretching bands in the ranges 910–945 and 894–912 cm^{-1} diagnostic of the Re=O stretching modes, and a strong absorption at *ca.* 670 cm^{-1} which may be assigned to Re–O–Re stretching. These values are comparable with literature data for analogous species.[20] Additionally, three strong bands are also found at 1280–1300 cm^{-1}, 1430–1440 cm^{-1} and *ca.* 1660 cm^{-1}, assigned to ν(CS) and ν(CN) of thiazole and ν(CO), respectively. All the ^{1}H NMR signals have been attributed to the respective protons (see Experimental section). In particular, the phosphinic methyl-proton resonances occur as two doublets at δ 1.5–1.6 and 1.9 (*J* = 13.6 Hz) while a singlet is observed in the ^{31}P{^{1}H}NMR spectra, suggesting equivalence of the two phosphines. The methyl groups of the two PMe$_2$Ph ligands are

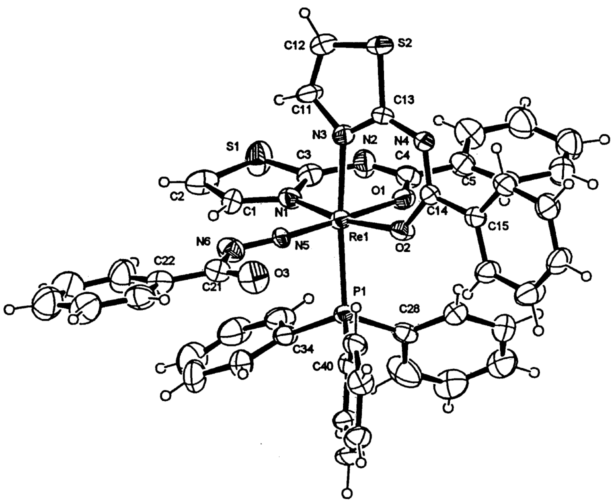
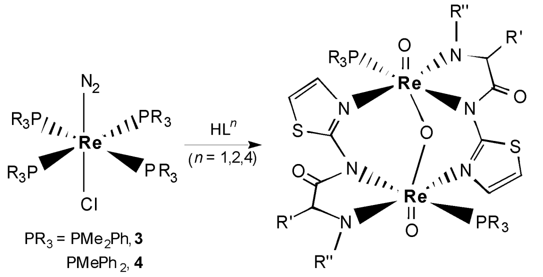


Fig. 3 An ORTEP view of complex **12** showing thermal ellipsoids at 30% probability.



PR$_3$ = PMe$_2$Ph, **3**
PMePh$_2$, **4**

PR$_3$ = PMe$_2$Ph, n = 1, **13**; n = 2, **14**; n = 4, **15**
PR$_3$ = PMePh$_2$, n = 2, **16**
R'' = -CO$_2$CH$_2$Ph, -CO$_2{}^t$Bu

Scheme 4

diastereotopic and different chemical shifts may be expected.[21] Also for these compounds, the –CHS and –CHN protons of the thiazolic ring are shifted upfield.[12e,f] These spectroscopic data, and the elemental analyses, are not sufficient to give an exact formulation for these compounds. Crystals suitable for an X-ray investigation were obtained for complex **14**. The structure shows a dinuclear species where two octahedral Re(v)-oxo units share a μ(O) oxygen, (Fig. 4, Table 4).

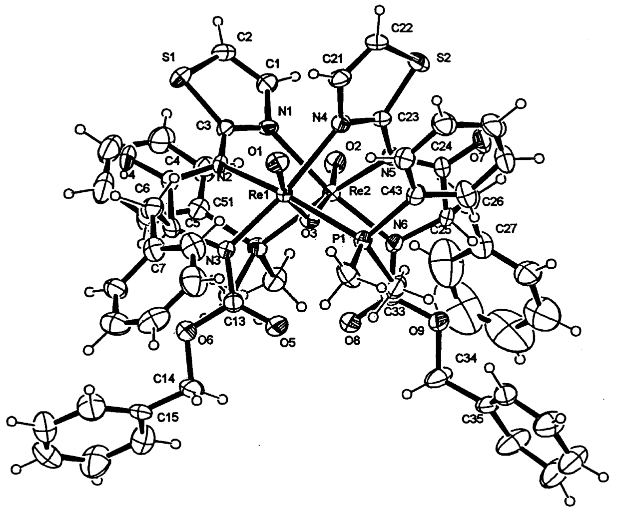


Fig. 4 An ORTEP view of complex **14** showing thermal ellipsoids at 30% probability.

Table 4 Selected bond distances (Å) and angles (°) for compound **14**

Re1–O1	1.690(7)	Re2–O2	1.684(7)
Re1–P1	2.462(2)	Re2–P2	2.464(3)
Re1–O3	1.925(7)	Re2–O3	1.897(7)
Re1–N2	2.075(7)	Re2–N5	2.078(9)
Re1–N3	2.028(8)	Re2–N6	2.025(7)
Re1–N4	2.280(9)	Re2–N1	2.282(8)
N1–C3	1.322(13)	N4–C23	1.344(14)
N2–C3	1.380(14)	N5–C23	1.357(14)
N2–C4	1.376(12)	N5–C24	1.375(12)
O4–C4	1.233(12)	O7–C24	1.231(13)
N3–C5	1.472(12)	N6–C25	1.481(12)
C4–C5	1.511(16)	C24–C25	1.519(16)
Re1–O3–Re2	138.3(4)	O2–Re2–O3	166.7(3)
O1–Re1–O3	165.7(3)	O2–Re2–P2	86.9(3)
O1–Re1–P1	86.8(2)	O2–Re2–N5	103.5(4)
O1–Re1–N2	103.8(4)	O2–Re2–N6	97.6(4)
O1–Re1–N3	97.9(4)	O2–Re2–N1	83.5(3)
O1–Re1–N4	82.7(4)	P2–Re2–O3	86.6(2)
P1–Re1–O3	86.4(2)	O3–Re2–N5	83.4(3)
O3–Re1–N2	83.8(3)	O3–Re2–N6	95.0(3)
O3–Re1–N3	95.6(3)	O3–Re2–N1	84.7(3)
O3–Re1–N4	86.4(2)	P2–Re2–N5	169.6(3)
P1–Re1–N2	169.3(3)	P2–Re2–N6	100.2(2)
P1–Re1–N3	99.9(2)	P2–Re2–N1	88.7(2)
P1–Re1–N4	88.3(2)	N5–Re1–N6	77.4(3)
N2–Re1–N3	77.2(3)	N5–Re1–N1	93.7(3)
N2–Re1–N4	94.8(3)	N6–Re2–N1	171.1(3)
N3–Re1–N4	171.9(3)	Re2–N1–C3	129.8(6)
Re1–N4–C23	130.4(6)	Re2–N5–C23	123.6(6)
Re1–N2–C3	124.7(6)	Re2–N5–C24	114.8(7)
Re1–N2–C4	115.2(7)	Re2–N6–C25	113.7(5)
Re1–N3–C5	112.7(6)	N4–C23–N5	122.3(9)
N1–C3–C2	122.3(7)	N5–C24–C25	113.9(8)
N2–C4–C5	113.3(8)	N6–C25–C24	109.0(7)
N3–C5–C4	109.3(8)		

This facile oxidation from Re(I) to Re(v) oxo-species by air was quite unexpected. Oxo-Re(v) complexes with this class of ligands were never isolated when oxo- or dioxo-rhenium(v) precursors were used.

The displacement of N$_2$ and/or oxidation of the metal seems to be governed by the experimental conditions employed as well as the properties of the HL^n ligand itself[10b,11d] and co-ligands. In fact, the precursor **2** gives rise to Re(II) species probably due to the presence of CO which is able to stabilize low oxidation states of the metal, while **3** and **4** do not contain suitable co-ligands.

Crystal structures

ORTEP[22] views of complexes **9**, **11**, **12** and **14** are represented in Figs. 1, 2, 3 and 4 respectively. Selected bond distances and angles are given in Tables 1, 2, 3 and 4.

In complex **9**, the overall geometry around the central Re1(II) atom is distorted octahedral. The principal reason for the distortion is the small bite angle of the deprotonated benzoyl-2-aminothiazole [O2–Re1–N2 = 84.31(8)°]. In this ligand the lengthening of the C2–O2 bond to 1.265(3) Å and the C–N bond distances, which are almost equivalent [C2–N1 = 1.328(4), C3–N1 = 1.343(4) and C3–N2 = 1.346(4) Å], indicate a delocalization of the double bonds and of the negative charge throughout the O2=C2–N1=C3–N2 moiety. The Re1–O2 distance of 2.132(2) Å shows an unusual lengthening with respect to the Re1–N2 of 2.087(2) Å because of the *trans* influence exerted by the carbonyl group on the O2 oxygen. The apical triphenylphosphines are *trans* to each other and display Re–P distances of 2.480(1) and 2.468(1) Å, which are typical for this co-ordination mode.[23,24]

Compound **11** is a Re(III) complex and contains, with respect to complex **9**, the benzoyldiazenido ligand (PhC(O)–N=N)$^-$ instead of the carbonyl group. The organodiazenido induces a further octahedral distortion evaluated by the widening of the N3–Re1–X(*cis*) mean angle of 93.8°. The short Re1=N3 [1.744(5) Å] and N3–N4 [1.284(7) Å] distances suggest the presence of two adjacent double bonds on the Re1=N3=N4–Ar unit, an observation confirmed by the linearity of the Re1=N3=N4 moiety [170.1(5)°]. These structural data are in perfect agreement with those observed in other rhenium organodiazenido complexes.[19,25–29] The co-ordinated benzoyl-2-aminothiazole ligand shows similar features to those observed in complex **9**, except for the Re1–O1 bond which displays a more usual distance of 2.045(4) Å which is shorter than Re1–N1 one of 2.116(5) Å, showing that the organodiazenido unit does not induce a *trans* influence.

Compound **12** is an analogous organodiazenido complex of Re(III) where the chlorine atom and a triphenylphosphine of complex **11** are substituted by a second deprotonated benzoyl-2-aminothiazole molecule. The two chelate rings are almost mutually orthogonal and their geometrical features are comparable to those observed in complexes **9** and **11**, except for the lengthening of the Re1–N3 distance to 2.134(8) Å which is due to the *trans* influence of the triphenylphosphine group. Accordingly the Re1–P distance is shortened to 2.406(3) Å owing to the absence of the other triphenylphosphine in a mutual *trans* position. The Re=N=N–Ar unit displays geometrical parameters in agreement with those observed in complex **11** [Re1–N5 = 1.753(8), N5–N6 = 1.28(1) Å, Re1–N5–N6 = 160.5(8)°] giving rise to an analogous octahedral distortion estimated by the N5–Re1–X(*cis*) mean angle of 94.1°.

Compound **14** is a dinuclear complex where two octahedral Re(V)-oxo units share a μ(O) oxygen. The basal co-ordination sites of each Re(V) atom are occupied by two deprotonated nitrogens of the ligand and by the neutral nitrogen of the aminothiazole of a second molecule of ligand. A molecule of dimethylphenylphosphine completes the basal co-ordination. Usually, the O=Re–O–Re=O backbone is linear,[20b,30–32] however, this structure represents one of the few cases[20a,33] where, for steric reasons, the Re–O–Re bridging unit is rather bent [Re1–O3–Re2 = 138.3(4)°]. The two Re(V)-oxo dimers are related by a two-fold non-crystallographic axis coincident with the bisector of the Re1–O3–Re2 angle. Re=O multiple bonds of 1.690(7) and 1.684(7) Å, and Re–μ(O) distances of 1.925(7) and 1.897(7) Å are in agreement with the values found in similar linear and bent complexes.[20a,b,30–33] Since the N2 and N5 atoms are in a *trans* position with respect to a dimethylphenylphosphine group, the Re1–N2 and Re2–N5 distances, 2.075(7) and 2.078(9) Å, respectively, display a lengthening with respect to Re1–N3 and Re2–N6, 2.028(8) and 2.025(7) Å. Furthermore, the Re1–N4 and Re2–N1 bonds, 2.280(9) and 2.282(8) Å, respectively, show a more significant lengthening because both the N4 and N1 nitrogens are neutral atoms while N2, N3, N5 and N6 are negatively charged.

Concluding remarks

We have prepared and characterized new rhenium complexes containing amino acids functionalized with 2-aminothiazole (HL^n). The reaction of the Re(I) precursor [ReN$_2$(CO)$_2$(PPh$_3$)$_2$Cl] **2** with HL^n led to Re(II) derivatives [Re(L^n)(CO)(PPh$_3$)$_2$Cl] **5**–**9** which represent examples of mononuclear species containing a monoanionic bidentate ligand. Moreover, unexpected dimeric oxo-(μ-oxo)-Re(V) species [Re$_2$(O)$_3$(L^n)$_2$(P)$_2$] (P = PMe$_2$Ph, *n* = 1, **13**; *n* = 2, **14**; *n* = 4, **15**. P = PMePh$_2$, *n* = 2, **16**) were obtained from reaction of HL^n and [ReN$_2$(P)$_4$Cl] (P = PMe$_2$Ph, PMePh$_2$). As shown by our crystallographic studies, these oxo-complexes are one of the few cases where, for steric reasons, the Re–O–Re bridging unit is bent rather than linear. Interaction of HL^n ligands with the Re(V) complex [Re(NNC(Ph)O)(PPh$_3$)$_2$Cl$_2$] **1** gave mono- or di-substituted Re(III) organodiazenido compounds of general formulation [Re(NNCOPh)(L)(PPh$_3$)$_2$Cl] or [Re(NNCOPh)(L)$_2$(PPh$_3$)], respectively. In conclusion, 2-aminothiazole seems to be a suitable fragment to form bifunctional chelating agents useful for preparing rhenium complexes in low oxidation states.

Experimental

Unless otherwise noted, all chemicals were reagent grade and used without further purification. The compounds [Re(NNC(Ph)O)(PPh$_3$)$_2$Cl$_2$][9] and [ReN$_2$(CO)$_2$(PPh$_3$)$_2$Cl][10b] were prepared following the methodologies herein described as well as literature methods. [ReN$_2$(P)$_4$Cl][10b] (P = PMe$_2$Ph, PMePh$_2$) and [ReO(PPh$_3$)$_2$Cl$_3$][34] were prepared according to literature procedures. Protected amino acids, in L configuration, were purchased from Inalco per la Nova Biochem, Milan, Italy. Elemental analyses were performed using a Carlo Erba Instruments model EA 1110 machine; FT-IR spectra were recorded in the range 4000–200 cm^{-1} on a Nicolet 510 P FT-IR instrument in KBr, using a Spectra-Tech collector diffuse reflectance accessory. Electrochemical measurements were carried out on dichloromethane solutions that contained 0.1 M tetra-n-butylammonium hexafluorophosphate (TBAH) as supporting electrolyte. $E_{1/2}$ values were referenced to a SCE electrode at room temperature and are uncorrected for junction potentials. Voltammetric experiments were performed with an Ecochemie Autolab PGstat 30 apparatus using a glassy carbon working electrode and a platinum wire auxiliary electrode. Proton spectra of CDCl$_3$ solutions of the compounds were examined on a Bruker AM 200 spectrometer with SiMe$_4$ as internal standard, ^{31}P{^{1}H} NMR on the same instrument with a 85% H$_3$PO$_4$ solution as external standard. Melting points were taken on a Reichert-Jung Termovar apparatus and are uncorrected. Conductivities were obtained at sample concentrations of *ca.* 1 × 10^{-4} M in CH$_2$Cl$_2$ solutions at room temperature with an Amel Model 134 conductivity meter. Electronic absorption spectra were obtained on a Perkin-Elmer Lambda 40 spectrophotometer, X-band EPR spectrum of **5** was recorded with a Bruker 220 SE spectrometer. Magnetic moment measurements were determined on a magnetic susceptibility balance, MSB-AUTO, Scherwood Scientific Ltd.

Synthesis of ligands

The ligands have been obtained following the methodologies previously described by us.[14] When benzoyl chloride was used instead of its corresponding carboxylic acid, addition of 4-methylmorpholine was required to neutralise the hydrochloric acid formed in the coupling reaction.

HL^1. (82%), mp 126–128 °C. (Found: C, 55.3; H, 4.85; N, 13.65; S, 10.7%. C$_{14}$H$_{15}$N$_3$O$_3$S requires C, 55.1; H, 4.95; N, 13.75; S, 10.5%); ν_{max}/cm^{-1} 3220 (NH), 1720, 1670 (CO); δ_H (CDCl$_3$) 1.5 (3H, d, C$_\alpha$HCH$_3$), 4.7 (1H, m, C$_\alpha$H), 5.1 (2H, m, CH$_2$Ph), 5.95 (1H, br s, C$_\alpha$HN*H*), 7.0 (1H, d, CHN), 7.3 (5H, m, Ph), 7.55 (1H, d, CHS), 13.4 (1H, br s, NH).

HL^2. (74%), mp 97–99 °C. (Found: C, 62.7; H, 5.1; N, 11.1; S, 8.25%. C$_{20}$H$_{19}$N$_3$O$_3$S requires C, 63.0; H, 5.0; N, 11.0; S, 8.4%); ν_{max}/cm^{-1} 3325 (NH), 1720, 1684 (CO); δ_H (CDCl$_3$) 3.1 (2H, m, C$_\alpha$HC*H*$_2$), 4.8 (1H, m, C$_\alpha$H), 5.1 (2H, m, CH$_2$Ph), 5.8 (1H, d, C$_\alpha$H N*H*), 6.95 (1H, d, CHN), 7.0–7.4 (10H, m, Ph), 7.5 (1H, d, CHS), 12.1 (1H, br s, NH).

HL^3. (76%), mp 147–149 °C. (Found: C, 48.5; H, 6.35; N, 15.35; S, 11.5%. C$_{11}$H$_{17}$N$_3$O$_3$S requires C, 48.7; H, 6.3; N, 15.5; S, 11.8%); ν_{max}/cm^{-1} 3200–3400 (NH), 1678 (CO); δ_H (CDCl$_3$) 1.45 (9H, s, CCH$_3$), 1.5 (3H, d, C$_\alpha$HCH$_3$), 4.6 (1H, m, C$_\alpha$H), 5.45 (1H, br s, C$_\alpha$H N*H*), 7.05 (1H, d, CHN), 7.6 (1H, d, CHS), 12.25 (1H, br s, NH).

HL^4. (50%), mp 124–126 °C. (Found: C, 59.0; H, 6.05; N, 11.95; S, 9.5%. C$_{17}$H$_{21}$N$_3$O$_3$S requires C, 58.8; H, 6.1; N, 12.1; S, 9.25%); ν_{max}/cm^{-1} 3240 (NH), 1707–1665 (CO); δ_H (CDCl$_3$) 1.4 (9H, s, CCH$_3$), 3.1 (2H, m, C$_\alpha$HCH$_2$), 4.7 (1H, m, C$_\alpha$H), 5.3 (1H, br d, C$_\alpha$H N*H*), 7.0 (1H, d, CHN), 7.0–7.3 (5H, m, Ph), 7.6 (1H, d, CHS), 11.8 (1H, br s, NH).

HL^5. (75%), mp 152–154 °C. (Found: C, 58.7; H, 3.9; N, 13.75; S, 15.55%. $C_{10}H_8N_2OS$ requires C, 58.8; H, 3.95; N, 13.7; S, 15.7%); ν_{max}/cm^{-1} 3100–3200 (NH), 1677 (CO); δ_H ($CDCl_3$) 7.0, 7.6, 8.1 (7H, m, CHN, Ph, CHS), 12.9 (1H, s, NH).

Synthesis of $[ReN_2(CO)_2(PPh_3)_2Cl]$ 2

To $[As(Ph)_4][ReO_4]$ (200 mg, 0.32 mmol in CH_2Cl_2, 10 cm^3) was added conc. HCl (20 cm^3) and the reaction mixture kept under vigorous stirring at room temperature until the organic phase became orange–red, probably due to the formation of oxo-pentachlororhenate(VI) anion.[35] Benzoylhydrazine (3.2 mmol) was added and a colour change to pale yellow was observed. After separation of the two phases, ethanol (2 cm^3) and PPh_3 (2.5 mmol) were added to the organic solution. The mixture was gently warmed until it became bright green. This solution contains the chelate complex $[Re(NNC(Ph)O)(PPh_3)_2Cl_2]$ **1**. A mixture of methanol–benzene (1 : 1, 40 cm^3) and PPh_3 (2.5 mmol) was added and the reaction mixture was heated under reflux for 45 min while carbon monoxide was bubbled through the solution. A pale yellow powder was formed during this time; it was filtered off and washed with EtOH and Et_2O to eliminate excess PPh_3. An aliquot of the product may be obtained from the concentrated mother solution. The identity of this product was based on a comparison of its spectroscopic properties and elemental analysis with those of an authentic sample.[10a] Yield > 85% based on starting rhenium salt.

Synthesis of Re(II) complexes $[Re(L^n)(PPh_3)_2(CO)Cl]$ 5–9 (n = 1–5)

A sample of the precursor $[ReN_2(CO)_2(PPh_3)_2Cl]$ **2** (100 mg, 0.12 mmol) in CH_2Cl_2–C_6H_6 (1 : 2v/v, 40 cm^3; alternatively, in C_6H_6, 40 cm^3) was treated with the appropriate ligand as a solid in 1 : 2 stoichiometric ratio and NEt_3 (1 cm^3) added. Within 10 min the yellow solution turned to red; the reaction mixture was refluxed for 6 h. The volume was reduced to *ca.* 1 cm^3 and an equal volume of diethyl ether and ethanol was added to induce precipitation. A red solid was filtered off, washed with ethanol (2 × 2 cm^3) and dried with Et_2O. Yields determined on the starting material ranged from 40% for **7** and **8** to 85% for **5**. As an example, a reaction was carried out with HL^5 in anhydrous benzene with Proton-Sponge [1,8-bis(dimethylamino)naphthalene] as deprotonating agent under a stream of dinitrogen. The corresponding complex **9** was collected in good yield (*ca.* 80%). Recrystallization of **9** from CH_2Cl_2–EtOH gave good quality crystals suitable for X-ray analysis.

$[Re(L^1)(PPh_3)_2(CO)Cl]$ 5. (85%), (Found: C, 56.7; H, 3.95; N, 3.7; S, 2.8%. $C_{51}H_{44}ClN_3O_4P_2ReS$ requires C, 56.8; H, 4.1; N, 3.9; S, 2.95%); ν_{max}/cm^{-1} 3424 (NH), 1836 (C≡O), 1723 $(CO)_{carbam.}$, 1530 $(CO)_{amidic.}$, 1491–1435 $(CN)_{thiaz.}$ and 1171 $(CS)_{thiaz.}$. $E_{1/2}$(ReIII/II couple) +0.630, $E_{1/2}$(ReII/I couple) −0.700 V, scan rate = 200 mV s^{-1}. λ_{max}/nm (CH_2Cl_2) 450 (ε/dm^3 mol^{-1} cm^{-1} 2500).

$[Re(L^2)(PPh_3)_2(CO)Cl]$ 6. (65%), (Found: C, 59.6; H, 4.0; N, 3.4; S, 2.6%. $C_{57}H_{48}ClN_3O_4P_2ReS$ requires C, 59.2; H, 4.2; N, 3.6; S, 2.8%); ν_{max}/cm^{-1} 3416 (NH), 1838 (C≡O), 1723 $(CO)_{carbam.}$, 1530 $(CO)_{amidic}$, 1499–1439 $(CN)_{thiaz.}$, 1173 $(CS)_{thiaz.}$ and 1092 (PPh_3). $E_{1/2}$(ReIII/II couple) +0.650, $E_{1/2}$(ReII/I couple) −0.730 V, scan rate = 200 mV s^{-1}.

$[Re(L^3)(PPh_3)_2(CO)Cl]$ 7. (40%), (Found: C, 55.6; H, 4. 5; N, 4.1; S, 2.9%. $C_{48}H_{46}ClN_3O_4P_2ReS$ requires C, 55.2; H, 4.5; N, 4.0; S 3.05%); ν_{max}/cm^{-1} 3434 (NH), 1829 (C≡O), 1713 $(CO)_{carbam.}$, 1505 $(CO)_{amidic.}$, 1435 $(CN)_{thiaz.}$ and 1171 $(CS)_{thiaz.}$. $E_{1/2}$(ReIII/II couple) +0.600, $E_{1/2}$(ReII/I couple) −0.750 V, scan rate = 100 mV s^{-1}.

$[Re(L^4)(PPh_3)_2(CO)Cl]$ 8. (40%), (Found: C, 57.8; H, 4.5; N, 3.7; S, 2.9%. $C_{54}H_{50}ClN_3O_4P_2ReS$ requires C, 57.5; H, 4.5; N, 3.75; S, 2.85%); ν_{max}/cm^{-1} 3430 (NH), 1840 (C≡O), 1713 $(CO)_{carbam.}$, 1530 $(CO)_{amidic.}$, 1495–1437 $(CN)_{thiaz}$ and 1171 $(CS)_{thiaz.}$.

$[Re(L^5)(PPh_3)_2(CO)Cl]$ 9. (60%), (Found: C, 57.5; H, 3.9; N, 2.8; S, 3.0%. $C_{47}H_{37}ClN_2O_2P_2ReS$ requires C, 57.7; H, 3.8; N, 2.85; S, 3.3%); ν_{max}/cm^{-1} 1825 ν(C≡O), 1524 $(CO)_{amidic}$, 1487 $(CN)_{thiaz.}$ and 1172 $(CS)_{thiaz.}$. $E_{1/2}$(ReIII/II couple) +0.580, $E_{1/2}$(ReII/I couple) −0.777 V, scan rate = 100 mV s^{-1}. λ_{max}/nm (CH_2Cl_2) 500 (ε/dm^3 mol^{-1} cm^{-1} 2080).

Synthesis of Re(III) complexes $[Re(NNCOPh)(L^{2,5})(PPh_3)_2Cl]$ 10, 11 and $[Re(NNCOPh)(L^5)_2(PPh_3)]$ 12

The green complex $[Re(NNC(Ph)O)(PPh_3)_2Cl_2]$ **1** (150 mg, 0.16 mmol) and HL^{2,5} (0.16 mmol) were dissolved in 15 cm^3 each of methanol and benzene, and NEt_3 (1 cm^3) added. The mixture was refluxed and stirred for 5 h and it was accomplished by a colour change from green to brown. The solvent was removed under vacuum and the resulting brown solid washed with ethanol (2 × 2 cm^3) and dried with diethyl ether. The same results were obtained when the reactions were performed in benzene (30 cm^3). Recrystallization from CH_2Cl_2 gave olive-green crystals of **10** and **11**. Following an identical procedure, the disubstituted complex **12** could be recovered when the reaction was carried out with two equivalents of ligand. Yields determined on the starting rhenium precursor were ≥80% for all the complexes.

$[Re(NNCOPh)(L^2)(PPh_3)_2Cl]$ 10. (85%), (Found: C, 59.5; H, 4.15; N, 5.6; S, 2.4%. $C_{63}H_{53}ClN_5O_4P_2ReS$ requires C, 60.05; H, 4.2; N, 5.55; S, 2.5%); ν_{max}/cm^{-1} 1722 $(CO)_{carbam.}$, 1635 $(CO)_{benzoyl}$, 1504 $(N{=}N)_{hydraz}$ and 1235 (benzoyl); δ_H ($CDCl_3$) 2.3 (1H, m, $C_\alpha HCH_2$), 2.7 (1H, m, $C_\alpha HCH_2$), 4.2 (1H, m, $C_\alpha H$), 5.0 (2H, s, CH_2Ph), 5.15 (1H, d, NH), 6.1 (1H, d, CHN), 6.8 (1H, d, CHS), 7.0–7.9 (45H, m, Ph); δ_P ($CDCl_3$) 4.0 (s).

$[Re(NNCOPh)(L^5)(PPh_3)_2Cl]$ 11. (90%), (Found: C, 58.65; H, 3.95; N, 5.1; S, 3.0%. $C_{53}H_{42}ClN_4O_2P_2ReS$ requires C, 58.8; H, 3.9; N, 5.2; S, 2.95%); ν_{max}/cm^{-1} 1635 $(CO)_{benzoyl}$, 1510 $(N{=}N)_{hydraz}$ and 1238 (benzoyl); δ_H ($CDCl_3$) 5.65 (1H, d, CHN), 6.2 (1H, d, CHS), 6.4–7.6 (40H, m, Ph); δ_P ($CDCl_3$) 4.0 (s).

$[Re(NNCOPh)(L^5)_2(PPh_3)]$ 12. (80%), (Found: C, 54.5; H, 3.45; N, 8.4; S, 6.25%. $C_{45}H_{34}N_6O_3PReS_2$ requires C, 54.7; H, 3.5; N, 8.5; S, 6.5%); ν_{max}/cm^{-1} 1635 $(CO)_{benzoyl}$, 1505 $(N{=}N)_{hydraz}$ and 1235 (benzoyl); δ_H ($CDCl_3$) 5.75 (1H, d, CHN), 6.2 (1H, d, CHS), 6.4–7.6 (40H, m, Ph); δ_P ($CDCl_3$) 11.3 (s).

Synthesis of Re(V) complexes $[Re_2O_3(L^n)_2(PMe_2Ph)_2]$ 13–15 (n = 1, 2, 4) and $[Re_2O_3(L^2)_2(PMePh_2)_2]$ 16

To a solution of the dinitrogen complex $[ReN_2(PMe_2Ph)_4Cl]$ **3** (100 mg, 0.12 mmol) in CH_2Cl_2–C_6H_6 (1 : 2, 40 cm^3) ligand as a solid (0.24 mmol) and NEt_3 (1 cm^3) were added. The resulting yellow solution was heated under reflux and stirred for *ca.* 30 h. After 15 min a colour change to yellow–brown was observed. The solvent was removed on a rotary evaporator. The brown residue was treated with EtOH to separate **14** and **15** as violet solids. Compound **14** was dried with Et_2O, while **15**, which is soluble in diethyl ether, was dried under vacuum. Complex **13** was soluble in ethanol and the solid could be precipitated from EtOH–H_2O solution and dried under vacuum with P_2O_5. Suitable crystals of **14** for X-ray determination were grown from a CH_2Cl_2–EtOH mixture. For comparison, **16** could be recovered from precursor **4** following the procedure indicated before but with a reaction time of 6 h. In the synthesis of **13**–**15**, a chromatographic analysis showed the formation of a by-product identified as the Re(III) complex $[Re(PMe_2Ph)_3Cl_3]$ which was isolated when the reactions were carried out in

Table 5 Crystal data

Compound	9	11	12	14
Formula	$C_{47}H_{37}ClN_2O_2P_2ReS$	$C_{53}H_{42}ClN_4O_2P_2ReS$	$C_{45}H_{34}N_6O_3PReS_2$	$C_{56}H_{56}N_6O_9P_2Re_2S_2$
M	977.44	1082.56	988.07	1445.53
System	Triclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$	$P2_12_12_1$
a/Å	9.7671(1)	20.8074(6)	10.4175(6)	14.9495(3)
b/Å	11.7999(2)	9.9213(2)	21.6210(18)	17.8488(4)
c/Å	19.8616(3)	23.4766(8)	18.4750(12)	21.3756(2)
α/°	76.5863(8)	90	90	90
β/°	89.1218(10)	108.775(1)	98.805(5)	90
γ/°	68.3395(9)	90	90	90
U/Å^3	2063.17(5)	4588.4(2)	4112.0(5)	5703.6(2)
Z	2	4	4	4
D_c/g cm^{-3}	1.573	1.567	1.596	1.695
T/K	293	293	293	293
μ/cm^{-1}	31.79	28.69	31.45	44.30
Unique reflections	11830	10883	6345	8629
R_{int}	0.045	0.055	0.048	0.065
Observed reflections [$I > 2\sigma(I)$]	10995	8217	4968	7129
R (observed reflections)	0.0303	0.0590	0.0649	0.0469
wR (all reflections)	0.0734	0.1209	0.1435	0.1103

anhydrous solvents and under a nitrogen stream. Complexes **13**–**15** were purified on a silica gel column and eluted with ethyl acetate–hexane (1 : 1v/v).

[Re$_2$O$_3$(L^1)$_2$(PMe$_2$Ph)$_2$] 13. (40%), (Found: C, 41.0; H, 3.8; N, 6.7; S, 5.0%. $C_{44}H_{48}N_6O_9P_2S_2Re_2$ requires C, 40.5; H, 3.7; N, 6.4; S, 4.9%); ν_{max}/cm^{-1} 1657 (CO$_{carbam}$, CO$_{amidic}$), 1437 (CN)$_{thiaz.}$, 1287 (CS)$_{thiaz.}$, 945, 912 (Re=O) and 671 (Re–O–Re); δ_H (CDCl$_3$) 1.5 (12H, m, PCH$_3$), 1.7 (6H, m, C$_\alpha$HCH$_3$), 4.6 (2H, m, C$_\alpha$H), 5.1 (4H, d, CH$_2$Ph), 6.2 (2H, br d, CHN), 6.6 (2H, br d, CHS), 7.2–7.5 (20H, m, Ph); δ_P (CDCl$_3$) −19.0 (s).

[Re$_2$O$_3$(L^2)$_2$(PMe$_2$Ph)$_2$] 14. (90%), (Found: C, 46.1; H, 3.85; N, 5.65; S, 4.5%. $C_{56}H_{56}N_6O_9P_2Re_2S_2$ requires C, 46.2; H, 3.9; N, 5.8; S, 4.3%); ν_{max}/cm^{-1} 1657 (CO$_{carbam.}$, CO$_{amidic}$), 1437 (CN)$_{thiaz.}$, 1281 (CS)$_{thiaz.}$, 910 (Re=O) and 671 (Re–O–Re); δ_H (CDCl$_3$) 1.5, 1.9 (12H, 2d, J = 13.6 Hz, PCH$_3$), 3.25 (4H, m, C$_\alpha$HCH$_2$), 4.0 (2H, m, C$_\alpha$H), 5.3 (4H, 2s, CH$_2$Ph), 6.6 (2H, d, CHN), 7.1–7.4 (32H, m, Ph, CHS); δ_P (CDCl$_3$) −21.0 (s).

[Re$_2$O$_3$(L^4)$_2$(PMe$_2$Ph)$_2$] 15. (<35%), (Found: C, 43.2; H, 4.25; N, 5.95; S, 4.25%. $C_{50}H_{60}N_6O_9P_2Re_2S_2$ requires C, 43.25; H, 4.35; N, 6.05; S, 4.6%); ν_{max}/cm^{-1} 1655 (CO$_{carbam.}$, CO$_{amidic}$), 1441 (CN)$_{thiaz.}$, 1300 (CS)$_{thiaz.}$, 934, 910 (Re=O) and 670 (Re–O–Re); δ_H (CDCl$_3$) 1.0 (18H, s, CCH$_3$), 1.6, 1.9 (12H, 2d, J = 13.6 Hz, PMe$_2$), 3.1 (4H, m, C$_\alpha$HCH$_2$), 3.6 (2H, m, C$_\alpha$H), 6.3 (2H, d, CHN), 6.7 (2H, d, CHS), 7.1–7.5 (20H, m, Ph); δ_P (CDCl$_3$) −21.0 (s).

[Re$_2$O$_3$(L^2)$_2$(PMePh$_2$)$_2$] 16. (55%), (Found: C, 50.1; H, 3.85; N, 5.2; S, 4.15%. $C_{66}H_{60}N_6O_9P_2Re_2S_2$ requires C, 50.2; H, 3.8; N, 5.3; S, 4.05%); ν_{max}/cm^{-1} 1659 (CO$_{carbam.}$, CO$_{amidic}$), 1437 (CN)$_{thiaz.}$, 1287 (CS)$_{thiaz.}$, 937, 894 (Re=O) and 695 (Re–O–Re); δ_H (CDCl$_3$) 2.0 (3H, s, PCH$_3$), 2.1 (3H, s, PCH$_3$), 3.1–3.5 (4H, m, C$_\alpha$HCH$_2$), 4.3 (2H, m, C$_\alpha$H), 5.1 (4H, s, CH$_2$Ph), 6.5 (2H, d, CHN), 7.0 (2H, d, CHS), 7.1–7.8 (40H, m, Ph); δ_P (CDCl$_3$) −10.0 (s).

Crystal structure determinations

All X-ray experiments were carried out at room temperature, 298 K, on a single crystal Nonius Kappa CCD diffractometer with Mo-Kα radiation. The intensities were corrected for absorption effects (SORTAV).[36] Direct methods (SIR92)[37] and subsequent Fourier difference syntheses were used for the solution of the structures. The structures were refined (SHELXL97)[38] with anisotropic thermal factors for all non-hydrogen atoms. The positions of hydrogen atoms were calculated. Further details of the structure determinations are given in Table 5.

CCDC reference numbers 179466–179469.

See http://www.rsc.org/suppdata/dt/b2/b201609p/ for crystallographic data in CIF or other electronic format.

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