Synthesis and Characterization of Five-co-ordinate Rhenium(III) Complexes with 2-(Diphenylphosphino)-ethanethiolate and Monothiolate Ligands. Crystal Structure of [Re($Ph_2PCH_2CH_2S$)$_2$($PhCH_2S$)]†

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A new series of five-co-ordinate rhenium(III) complexes containing the mixed S,P-bidentate 2-(diphenylphosphino)ethanethiolate ligand together with a monothiol RSH [R = $Ph_2PCH_2CH_2$, $Ph_2P(O)CH_2CH_2$, $PhCH_2$, Ph or Pr^n] have been synthesized and characterized. This Re$^{III}P_2S_3$ series was prepared by substitution reactions of [Re$^{III}Cl_3(MeCN)(PPh_3)_2$], a pre-reduced rhenium(III) precursor, by addition of 2-(diphenylphosphino)ethanethiol and the corresponding monothiol. Formation of these compounds was verified by elemental analysis and ^1H and ^{31}P NMR and positive-ion fast atom bombardment mass spectroscopy. The complexes were found to be diamagnetic, neutral and stable. They exhibit a trigonal-bipyramidal geometry, where three sulfur atoms occupy the equatorial plane and two phosphorus atoms are positioned at the apices. The X-ray structural analysis of bis[2-(diphenylphoshino)ethanethiolato-κ*S*,κ*P*](phenylmethanethiolato-κ*S*)rhenium(III) revealed that this compound crystallizes in the monoclinic space group $P2_1/c$ with $Z = 8$, $a = 21.011(9)$, $b = 20.397(9)$, $c = 16.289(7)$ Å, $\beta = 107.13(5)°$, $R = 0.050$, $R' = 0.063$, by using 5644 observed reflections. The above data further demonstrate the preference of a five-co-ordinate configuration when the P_2S_3 donor-atom set is available for co-ordinating rhenium(III).

Rhenium and technetium are generally studied together, due to their similar chemical properties as elements of Group 7, and the development of ^{99m}Tc and $^{186/188}$Re radiopharmaceuticals, used in nuclear diagnosis and therapy respectively, has brought new interest in their chemistry.[1-4] Our recent work involves the study of phosphine derivatives, using other functional groups such as –CHO, –COOH, –OH, –NH_2 or –SH, as ligands for technetium and/or rhenium.[5-9] Combinations of monodentate phosphines with ligands containing several functional groups have been thoroughly studied with respect to technetium and rhenium.[10-13] As a further task, we were interested in investigating the role of the chelating effect involved in the formation and stability of these complexes when the above functional groups and the phosphine belong to the same molecule.

Of particular interest are combinations of phosphine with thiolate soft-donor groups. These combinations lead usually to the formation of stable complexes with the metal in the +3 oxidation state. In this state technetium and rhenium exhibit a d^4 electronic configuration combined with an octahedral or trigonal-prismatic, or trigonal-bipyramidal geometry and accordingly co-ordination numbers of five or six are possible. The five-co-ordinate complexes so far reported always contain the S_3 atom set with two π back-bonding groups, one of which is usually a phosphine.[5,10,12-14] Six-co-ordinate complexes containing the S_3 atom set have also been reported. However, they are either less stable, or are stabilized by the chelating effect imposed by ligands with the proper electronic and/or spatial characteristics.[5,15]

A Tc$^{III}P_2S_3$ five-co-ordinate complex with the 2-(diphenylphosphino)ethanethiolate ligand has recently been described.[16] In this complex one of the three co-ordinating ligand molecules is present as a monodentate thiol, while the remaining phosphorus atom is present as non-co-ordinating, oxidized phosphorus(V) (–P=O).[16]

We report here the synthesis and physicochemical characteristics of a new series of five-co-ordinate Re$^{III}P_2S_3$ complexes, containing the 2-(diphenylphosphino)ethanethiolate ligand together with a monothiol RSH, where R = $Ph_2PCH_2CH_2$, $Ph_2P(O)CH_2CH_2$, $PhCH_2$, Ph or Pr^n. The X-ray crystal structure of bis[2-(diphenylphosphino)ethanethiolato-κ*S*,κ*P*]-(phenylmethanethiolato-κ*S*)rhenium(III) is also reported.

Results and Discussion

A series of five-co-ordinate rhenium(III) complexes of the general formula Re$^{III}P_2S_3$ have been synthesized. This series was generated from pre-reduced [Re$^{III}Cl_3(MeCN)(PPh_3)_2$] **2** by substitution reactions with mixed bidentate 2-(diphenylphosphino)ethanethiol and monodentate thiol ligands, according to equation (1). Attempts to obtain the same compounds starting

$$[\mathrm{Re^{III}Cl_3(MeCN)(PPh_3)_2}] + x\mathrm{Ph_2PCH_2CH_2SH} + y\mathrm{RSH} \longrightarrow [\mathrm{Re^{III}(Ph_2PCH_2CH_2S)_2(RS)}] \quad (1)$$

from rhenium-(VII) or -(V) precursors by reduction/substitution reactions with $Ph_2PCH_2CH_2SH$ failed. However, this synthetic route has been successfully followed for preparing the Tc$^{III}P_2S_3$ analogue with $Ph_2PCH_2CH_2SH$,[16] as a result of the greater tendency of technetium to be reduced as compared with rhenium.[3] The preparation of the new compounds **3**–**7** is described in Scheme 1, while positive-ion fast atom bombardment (FAB$^+$) mass and NMR spectroscopic data are summarized in Table 1. All the Re$^{III}P_2S_3$ complexes exhibited a similar geometric configuration, in which the three sulfur atoms occupy the equatorial plane and the two phosphorus atoms the apices of a trigonal bipyramid. Neutral compounds were formed in all cases, since the three thiol groups are deprotonated upon co-ordination with Re^{3+}, while the two phosphorus atoms remain neutral. The Re$^{III}(Ph_2PCH_2CH_2S)_2{}^+$ part of the structure remains the same throughout

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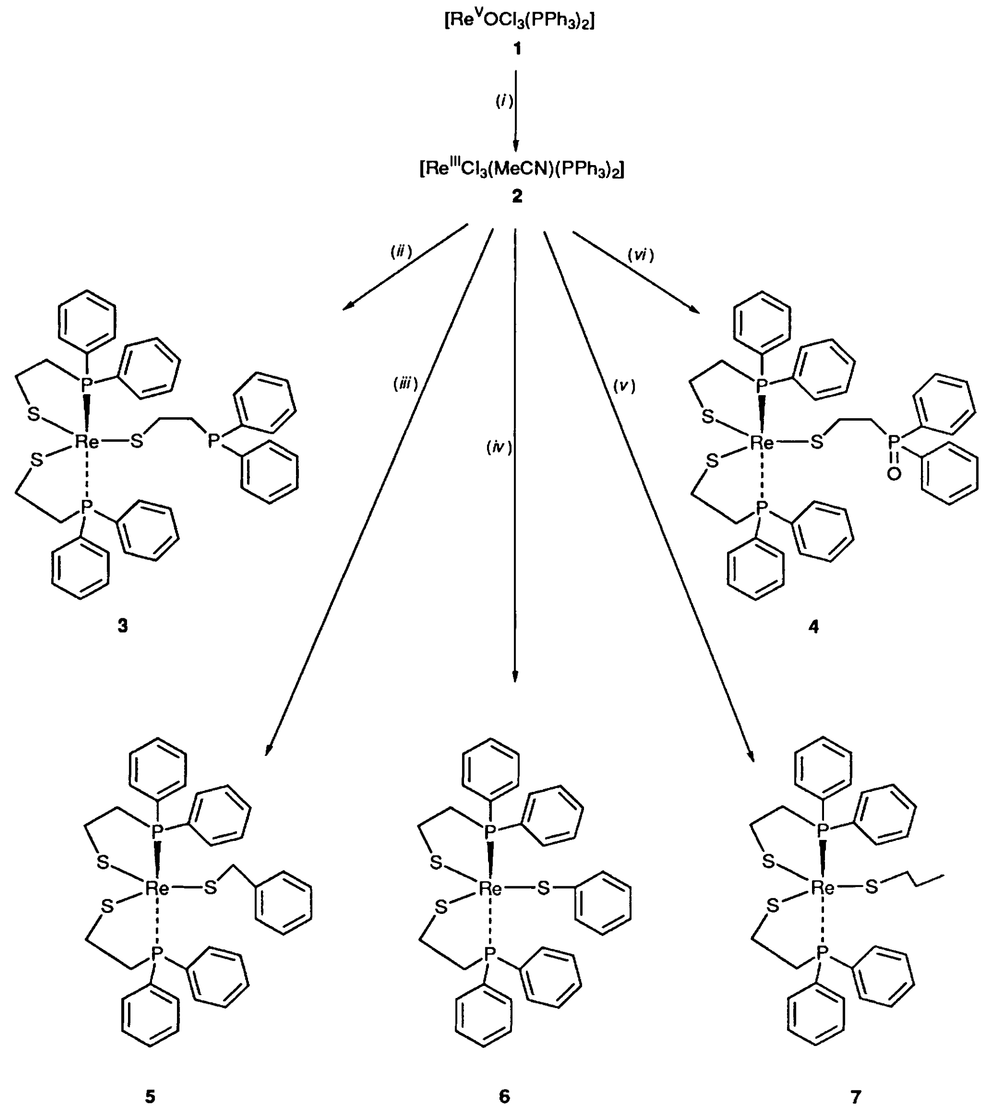
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.



Scheme 1 (*i*) PPh$_3$, MeCN–toluene; (*ii*) 4 Ph$_2$PCH$_2$CH$_2$SH, argon–EtOH–toluene; (*iii*) Ph$_2$PCH$_2$CH$_2$SH:PhCH$_2$SH, 3:5, nitrogen–EtOH–toluene; (*iv*) Ph$_2$PCH$_2$CH$_2$SH:PhSH, 3:5, nitrogen–EtOH–toluene; (*v*) Ph$_2$PCH$_2$CH$_2$SH:Pr^{n}SH, 3:5, argon–MeOH–benzene; (*vi*) 4 Ph$_2$PCH$_2$CH$_2$SH, EtOH–toluene

Table 1 NMR and FAB$^+$ mass spectroscopic data of the new compounds

	NMR					
	^{31}P		^{1}H			
Compound	P^{III}	P^V	Aromatic	Aliphatic	SH	FAB$^+$, *m/z* (relative intensity in %)
Ph$_2$PCH$_2$CH$_2$SH	−20.0	—	7.3–7.5 (m)	2.6 (m), 2.4 (m)	1.7 (dt)	—
[Re^{V}OCl(Ph$_2$PCH$_2$CH$_2$S)$_2$]	23.9	—	6.9–7.6 (m)	3.9 (m), 3.7 (m), 3.3 (m), 3.1 (m), 2.5 (m)	—	—
3	57.7 (br s), −16.0 (s)	—	7.1–7.5 (m)	2.8 (br s), 2.2 (br s), 1.9 (br s)	—	922 (M^+), 709 (M^+ − Ph$_2$PCH$_2$CH$_2$)
4	58.0 (d)	28.0 (s)	7.1–7.5 (m)	2.8 (br s), 2.2 (br s), 1.9 (br s)	—	938 (M^+), 709 [M^+ − Ph$_2$P(O)CH$_2$CH$_2$]
5	57.5 (s)	—	6.7–7.7 (m)	3.4 (s), 2.9 (m), 2.9 (m), 2.5 (m), 2.3 (m), 1.8 (m)	—	800 (M^+), 709 (M^+ − PhCH$_2$)
6	57.4 (s)	—	6.6–7.6 (m)	2.8 (m), 2.6 (m), 2.2 (m), 1.8 (m)	—	786 (100, M^+), 709 (71, M^+ − Ph)
7	57.9 (s)	—	6.9–7.7 (m)	2.8 (m), 2.6 (m), 2.3 (m), 2.0 (m), 1.6 (s), 1.1 (m), 0.4 (t)	—	751 (17, M^+), 709 (100, M^+ − Pr^n)

the $Re^{III}P_2S_3$ series, whereas the thiolate moiety occupying the fifth co-ordination site varies from compound to compound.

Despite these apparent similarities, the formation and stability of the $Re^{III}P_2S_3$ complexes synthesized depended upon the type of monodentate thiol ligand used. Compound **3** was obtained in good yields (70%) by treating compound **2** with $Ph_2PCH_2CH_2SH$ ($x = 4, y = 0$) only under strictly anaerobic conditions in a 1:4 molar ratio. However, at lower molar ratios ($x < 4$) the reaction yields dropped dramatically and a mixture of unidentified green intermediates containing PPh_3 were recovered.

The structure shown in Scheme 1 was attributed to **3** according to the elemental analysis and the spectroscopic data. The FAB^+ mass spectrum (Table 1) revealed a parent peak at *m/z* 922, consistent with this formula, where all three phosphorus atoms are non-oxidized P^{III}. The UV/VIS spectrum showed a band at 446 nm characteristic of Re^{III}–S charge-transfer bond(s), as reported for analogous rhenium(III)–thiolato complexes.[17] The IR spectrum, while confirming the presence of the S-thiolate, did not clearly demonstrate characteristic bands of metal–ligand vibrations. Therefore, it was only used as a 'fingerprint' for the other members of this series by locating additional 'characteristic' bands in each case, without, however, attributing them to a particular vibration.

From the ^1H and ^{31}P NMR data (Table 1) **3** was found to be diamagnetic, suggesting for rhenium(III) a d^4 configuration in a trigonal-bipyramidal field. Briefly, the ^1H NMR spectrum showed a multiplet at δ 7.3 attributed to the aromatic protons, a diffused multiplet at δ 2.8 generated by the three CH_2–S, and two more multiplets at δ 2.2 and 1.9 attributed to the methylene protons of the two co-ordinating and the remaining non-co-ordinating phosphorus atoms respectively. The complete assignment of the methylene proton peaks is difficult, because of their increased multiplicity. However, comparison with the free thiol peaks (Table 1) and integration of the protons confirmed the attributed formula. This formula was further verified by the ^{31}P NMR data (Table 1) revealing two peaks at δ 57.7 and −16.0. By comparison with the spectrum of the free thiol (Table 1), the first peak was attributed to two magnetically equivalent co-ordinating phosphorus(III) atoms in a *trans* position and the latter one to the non-co-ordinating third phosphorus(III) atom.

When the reaction conditions were not strictly anaerobic, the yield of formation of **3** decreased and instead complex **4** precipitated from the reaction mixture. It was found that formation of **4** depended on the amount of pre-oxidized 2-(diphenylphosphino)ethanethiol present. By using old, partially oxidized batches of the thiol, the formation of **4** increased dramatically. On the contrary, by exposing solutions of **3** to the air, no oxidation of the non-co-ordinating P^{III} to P^V was observed. Instead, **3** was preferentially oxidized on the metal site, forming $[Re^VOCl(Ph_2PCH_2CH_2S)_2]$. The highest yield of **4** was obtained from reaction (1) when R = Pr^n, $x = 3$ and $y = 5$.

Analytical data obtained for complex **4** are almost identical to those of **3** (Table 1). However, the presence of the P=O group was evident in most of the spectroscopic characterizations. The FAB^+ mass spectrum revealed a parent peak at *m/z* 938, 16 atomic mass units higher, confirming the presence of an additional oxygen atom. The IR spectrum demonstrated an additional band at 1187 cm^{-1}, attributed to ν(P=O), and a small but significant peak at 714 cm^{-1}, assigned to bending vibrations of this group. Eventually, the strongest evidence for the formation of **4** was obtained from the ^{31}P NMR spectrum (Table 1). The spectrum showed two peaks. One at δ 58.0 corresponding to the two co-ordinating P^{III} atoms at the same position as for **3** and the second at δ 28.0 and therefore shifted 44.0 ppm in comparison to the third P^{III} atom of **3**. This peak was attributed to a P^V=O atom, by comparison with the oxidized free thiol signal (δ 30.8) and the one from the analogous Tc^{III} complex (δ 27.7).[16]

It is evident that reaction of the thiol with the rhenium(III) precursor clearly leads to the formation of the $Re^{III}P_2S_3$ species, where the thiol is present twice as a bidentate phosphinethiolate and once as a monodentate thiolate ligand. In this instance, a five-co-ordinate complex exhibiting trigonal-bipyramidal geometry is the most stable product. However, when other bidentate phosphinethiolate ligands are used, *e.g.* 2-(diphenylphosphino)benzenethiolate, six-co-ordinate $Re^{III}S_3P_3$ compounds form, exhibiting an octahedral configuration.[5,15] Therefore, the ligand with its particular characteristics, nucleophilicity, size, rigidity, delocalization of electrons in the final complex, seems to be responsible in the selection of the most favourable geometry.

At this point, substitution of the monodentate thiol of the $Re^{III}P_2S_3$ complex with a series of other monodentate thiol ligands was investigated. However, all attempts to substitute the thiolate moiety starting either from **3** or from **4**, using various aliphatic or aromatic thiols and varying the reaction conditions (pH, time, molar ratio of reactants, solvent) failed, leading either to the recovery of the starting material, or, under drastic conditions, to a mixture of decomposition products of the parent compound. The $Re^{III}P_2S_3$ species, once created, proved to be extremely stable.

Therefore, preparation of the mixed-ligand $Re^{III}P_2S_3$ complexes **5**–**7** was finally achieved by using $[Re^{III}Cl_3(MeCN)(PPh_3)_2]$ as the starting compound, according to equation (1). High yields (>70%) were readily obtained at molar ratios $x = 3$ and $y = 5$. In fact, by using less excess of thiol ($y < = 5$), mixtures of unidentified green intermediates containing PPh_3, as well as oxidized compound **4** formed. The use of less $Ph_2PCH_2CH_2SH$ ($x < 3$) led equally to a mixture of non-characterized, green compounds. Complexes **5**–**7** showed similar spectroscopic features. All three UV/VIS spectra were identical with those of **3** and **4**, demonstrating that the observed bands originated predominantly from Re^{III}–S electronic transitions and that the internal electronic density was not influenced by changing R. The IR spectra also showed a similar pattern.

The FAB^+ mass, ^1H and ^{31}P-NMR data, summarized in Table 1, verify the expected structure of these complexes. A common feature in the FAB^+ mass spectra of all the $Re^{III}P_2S_3$ complexes is the presence of a daughter peak at *m/z* 709, corresponding to the $Re(Ph_2PCH_2CH_2S)_2SH^+$ fragment. This is a further demonstration of the high stability of the $Re^{III}P_2S_3$ moiety. All complexes were diamagnetic, as expected for a trigonal-bipyramidal d^4 configuration. The ^{31}P NMR spectra were identical for compounds **5**–**7**, demonstrating a peak at *ca.* δ 58.0. This peak was attributed to the two co-ordinating P^{III} atoms present in all three complexes and in accordance with the data obtained from **3** and **4**. Despite their complexity, the ^1H NMR spectra verified the presence of characteristic peaks of the co-ordinating monodentate thiol ligands in each complex. In particular, the characteristic chemical shift of the methylene protons of the $PhCH_2S$ group in **5** are found at δ 3.4 and therefore are shifted 0.6 ppm with respect to free $PhCH_2SH$ (δ 4.0), upon co-ordination with Re^{III}. For the same reason, the methyl protons of the Pr^nS group in **7** present as a triplet at δ 0.40 are shifted 0.16 ppm with respect to the free Pr^nSH (at δ 0.56). In addition, the ratio of aromatic/aliphatic protons, estimated after integration, confirmed in all cases the expected formulae.

The stability of the final product is the driving force towards selected formation of the $Re^{III}P_2S_3$ complex, when a mixture of ligands (neutral and oxidized $Ph_2PCH_2CH_2SH$ and monothiolate) co-exist in the reaction solution. Under the above conditions the major end product is **4**, which is consequently the most stable of the series. In the absence of oxidized $Ph_2PCH_2CH_2SH$ (strictly anaerobic conditions) compound **3** forms instead. Compounds **5**–**7** can only be obtained in the presence of non-oxidized $Ph_2PCH_2CH_2SH$ and when using a high excess of the corresponding monothiol. Therefore, the

Table 2 Atomic coordinates (× 10^4)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Re(1)	−3946(1)	1090(1)	3390(1)	Re(2)	935(1)	1012(1)	2204(1)
S(1)	−3577(2)	1838(2)	2638(2)	S(1′)	1685(2)	218(2)	2706(3)
S(2)	−3254(2)	219(2)	3752(3)	S(2′)	1061(2)	1908(2)	3047(3)
S(3)	−4978(2)	1185(2)	3559(2)	S(3′)	32(2)	871(2)	1057(2)
P(1)	−4469(2)	611(2)	2042(2)	P(1′)	1728(2)	1429(2)	1545(3)
P(2)	−3277(2)	1524(2)	4708(2)	P(2′)	328(2)	588(2)	3099(2)
C(1)	−3809(9)	1613(7)	1478(10)	C(1′)	2447(8)	346(7)	2399(11)
C(2)	−3972(8)	859(7)	1354(9)	C(2′)	2530(6)	1086(7)	2147(9)
C(3)	−2563(8)	390(7)	4754(10)	C(3′)	676(8)	1757(8)	3944(9)
C(4)	−2459(6)	1116(7)	4899(10)	C(4′)	684(9)	1000(8)	4133(9)
C(5)	−5061(8)	1631(9)	4509(10)	C(5′)	94(8)	1145(9)	−2(9)
C(6)	−5781(7)	1660(7)	4498(9)	C(6′)	−543(8)	1455(7)	−516(9)
C(7)	−6239(7)	2091(7)	4001(9)	C(7′)	−649(9)	2124(8)	−454(11)
C(8)	−6890(9)	2108(8)	4047(10)	C(8′)	−1233(9)	2430(10)	−941(11)
C(9)	−7074(10)	1697(9)	4556(11)	C(9′)	−1719(9)	2066(8)	−1518(10)
C(10)	−6648(10)	1264(10)	5039(12)	C(10′)	−1618(8)	1391(8)	−1603(10)
C(11)	−5983(9)	1231(8)	5028(11)	C(11′)	−1043(7)	1102(8)	−1107(9)
C(12)	−5299(7)	900(7)	1423(9)	C(12′)	1689(7)	1180(7)	438(8)
C(13)	−5790(8)	493(9)	959(10)	C(13′)	1728(7)	1623(7)	−186(9)
C(14)	−6407(9)	731(9)	458(11)	C(14′)	1694(8)	1417(8)	−1019(10)
C(15)	−6495(10)	1408(9)	448(12)	C(15′)	1613(8)	764(8)	−1213(11)
C(16)	−5989(9)	1837(9)	912(10)	C(16′)	1564(8)	303(9)	−599(10)
C(17)	−5434(8)	1578(8)	1405(10)	C(17′)	1608(7)	515(7)	233(9)
C(18)	−4530(7)	−281(7)	1961(9)	C(18′)	1893(7)	2312(7)	1550(9)
C(19)	−4471(8)	−627(9)	1236(11)	C(19′)	2553(8)	2544(8)	1729(10)
C(20)	−4537(10)	−1308(10)	1234(13)	C(20′)	2656(10)	3232(9)	1781(11)
C(21)	−4676(8)	−1651(9)	1879(11)	C(21′)	2123(10)	3643(10)	1618(11)
C(22)	−4724(8)	−1309(8)	2593(11)	C(22′)	1468(9)	3409(9)	1435(10)
C(23)	−4672(7)	−624(7)	2612(10)	C(23′)	1375(8)	2746(8)	1413(10)
C(24)	−3082(7)	2411(7)	4812(9)	C(24′)	−549(7)	778(7)	2894(9)
C(25)	−2431(9)	2651(9)	5217(11)	C(25′)	−812(8)	1348(8)	2479(10)
C(26)	−2356(10)	3227(9)	5203(12)	C(26′)	−1506(9)	1500(10)	2346(12)
C(27)	−2835(9)	3730(9)	4828(11)	C(27′)	−1871(11)	1086(10)	2651(12)
C(28)	−3485(9)	3516(8)	4427(10)	C(28′)	−1642(10)	552(10)	3048(12)
C(29)	−3598(8)	2834(7)	4428(9)	C(29′)	−980(9)	374(9)	3190(11)
C(30)	−3472(7)	1284(6)	5698(8)	C(30′)	367(7)	−291(7)	3327(9)
C(31)	−3290(7)	1647(7)	6452(8)	C(31′)	563(8)	−536(8)	4175(11)
C(32)	−3427(7)	1414(8)	7175(10)	C(32′)	604(10)	−1225(10)	4269(13)
C(33)	−3729(7)	834(7)	7165(10)	C(33′)	433(9)	−1616(10)	3614(12)
C(34)	−3920(8)	446(8)	6430(9)	C(34′)	206(10)	−1390(10)	2771(13)
C(35)	−3800(8)	689(8)	5682(10)	C(35′)	212(8)	−711(9)	2658(11)

stability of the mixed-ligand complexes **5**–**7** is less than that of **3** and **4**.

The identification of the atoms and the crystal structure of **5** is shown in Fig. 1. Fractional atomic coordinates are given in Table 2 and selected bond lengths and angles in Table 3. Complex **5** consists of two monomeric, neutral, independent and well separated $Re(Ph_2PCH_2CH_2S)_2(PhCH_2S)$ moieties (A and B); there is no intermolecular bonding of significance and in both moieties the co-ordination geometry about the metal is trigonal bipyramidal with equatorial uninegative thiolate ligands, the metal atoms being displaced from the equatorial plane by 0.10 Å. Apart from the orientation of the $PhCH_2S^-$ ligand, the torsion angle Re(1)S(3)C(5)C(6) is 178.4 in A and − 140.9° in B, the moieties are roughly superimposable (Fig. 2). In fact, the weighted root-mean-square deviation, derived from the BMFIT program,[19] is 0.17 Å, when the fitting is performed using the co-ordination geometry atoms. Nevertheless, no bond distances and angles differ by more than two standard deviations. Therefore, further discussion on distances and angles will refer to the mean value of molecules A and B. Despite the different $PhCH_2S$ orientations, in both molecules the benzyl ring is practically parallel to the equatorial plane of the complex; the pertinent dihedral angles are 16.1 (A) and 15.5° (B). Upon co-ordination of the bidentate phosphinethiolate ligands the carbon atoms attached to the phosphorus are out-of-plane of the five-membered rings by 0.67 and 0.68 and 0.59 and 0.76 Å in A and B respectively; the dihedral angle between the two five-membered rings is 72.6 in A and 68.2° in B. In the equatorial plane the Re–S average distance is 2.253(4) Å and the S–Re–S angle 119.8(2)°. These values are in good agreement with the data in Table 4, where some relevant entities of similar five-co-ordinate rhenium(III) complexes containing sulfur and phosphorus donor atoms are reported. The two bidentate phosphinethiolate $Ph_2PCH_2CH_2S$ ligands co-ordinate through the sulfur atom in the equatorial plane and the phosphorus atom in the axial position, while the phenylmethanethiolate ligand through the S(3) atom completes the equatorial plane. In this way, a trigonal-bipyramidal geometry results, with a P–Re–P angle of 170.5° and the mean of the equatorial S–Re–S angles approximately 120°.

The trigonal-bipyramidal geometry was to be expected. In fact, the geometry, trigonal bipyramidal or square pyramidal, is dictated by the steric characteristics of the co-ordinating ligand(s). The presence of bulky ligands, such as phosphines, favours a trigonal-bipyramidal geometry (Table 4). On the other hand, π-donating groups located in axial positions, in particular the ones whose electronic distribution exhibits cylindrical symmetry, *e.g.* oxo or nitrido groups, results in a square-pyramidal configuration where the rhenium is above the basal plane and towards the π-donating group. A comparison of the Re–S distances of the three rhenium(III) complexes (Table 4) containing the S_3-co-ordinating set reveals in all three cases the perfect coincidence of those values. Therefore, modifications of the ligand 'backbone' do not seem to interfere with the electronic density of the metal and its co-ordinating groups.

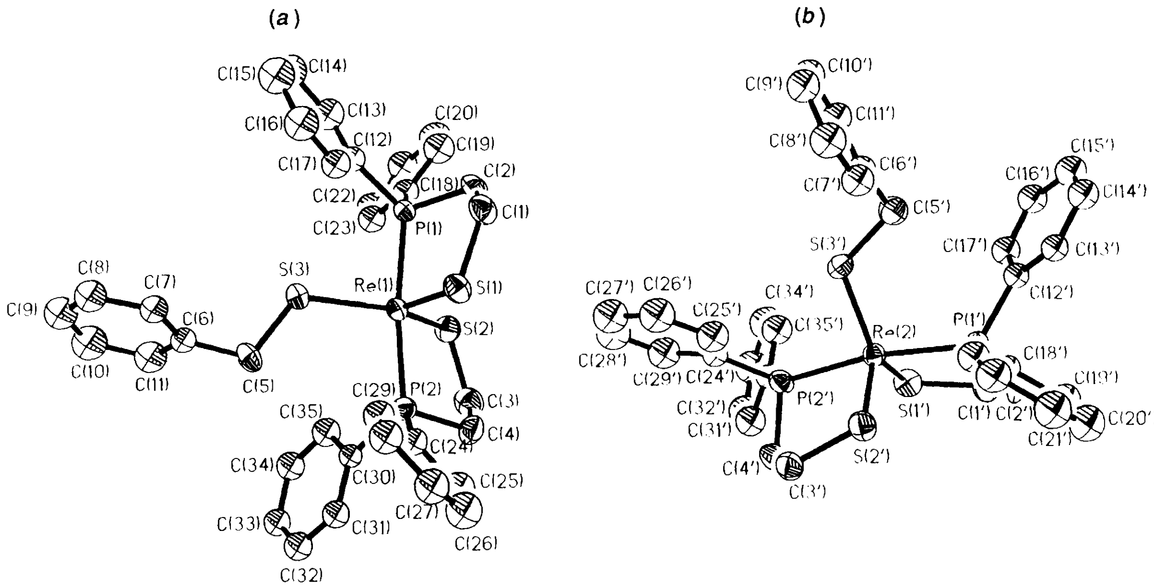


Fig. 1 An ORTEP[18] diagram of the two molecules A (*a*) and B (*b*) in complex **5**, showing the atom labelling scheme; the thermal ellipsoids are drawn at 50% probability and the hydrogen atoms are omitted for clarity

Table 3 Selected distances (Å) and angles (°)

	Molecule A	Molecule B
Re–S(1)	2.236(4)	2.239(4)
Re–S(2)	2.262(4)	2.254(4)
Re–S(3)	2.272(4)	2.255(4)
Re–P(1)	2.359(4)	2.387(5)
Re–P(2)	2.365(4)	2.364(5)
S(1)–C(1)	1.86(2)	1.83(2)
C(1)–C(2)	1.58(2)	1.58(2)
P(1)–C(2)	1.82(2)	1.82(1)
S(2)–C(3)	1.87(1)	1.89(2)
C(3)–C(4)	1.50(2)	1.57(2)
P(2)–C(4)	1.85(1)	1.83(1)
P(1)–C(12)	1.84(1)	1.85(1)
P(1)–C(18)	1.83(1)	1.83(1)
P(2)–C(24)	1.85(2)	1.83(2)
P(2)–C(30)	1.84(1)	1.83(1)
S(3)–C(5)	1.85(2)	1.85(2)
C(5)–C(6)	1.51(2)	1.50(2)
S(1)–Re–S(2)	112.2(2)	114.8(1)
S(1)–Re–S(3)	120.4(1)	122.7(1)
S(1)–Re–P(1)	85.1(1)	85.0(2)
S(1)–Re–P(2)	91.8(1)	87.7(2)
S(2)–Re–S(3)	126.8(2)	121.8(2)
S(2)–Re–P(1)	90.2(1)	90.7(2)
S(2)–Re–P(2)	83.8(1)	84.7(2)
S(3)–Re–P(1)	87.1(1)	101.6(1)
S(3)–Re–P(2)	101.1(1)	89.4(1)
P(1)–Re–P(2)	171.8(2)	168.9(1)
Re–S(1)–C(1)	111.0(6)	112.0(5)
S(1)–C(1)–C(2)	110.6(10)	112.2(11)
C(1)–C(2)–P(1)	109.6(12)	110.5(9)
Re–S(2)–C(3)	110.8(5)	109.8(5)
S(2)–C(3)–C(4)	111.1(9)	109.2(12)
C(3)–C(4)–P(2)	109.3(10)	107.0(9)
Re–S(3)–C(5)	118.2(5)	117.4(5)
Re–P(1)–C(2)	105.3(5)	106.2(5)
Re–P(1)–C(18)	118.9(5)	120.3(6)
Re–P(2)–C(4)	105.0(5)	104.6(6)
Re–P(2)–C(24)	120.3(4)	120.8(5)
Re–P(2)–C(30)	117.9(4)	118.9(6)

Conclusion

A new series of five-co-ordinate $Re^{III}P_2S_3$ complexes containing the 2-(diphenylphosphino)ethanethiolate ligand have been prepared and characterized. These compounds were obtained by substitution reactions of a rhenium(III) precursor and could not form from $Re^{V/VII}$ by reduction/substitution reactions. The $(Ph_2PCH_2CH_2S)_2Re^{III}$ moiety, a combination of two 2-(diphenylphosphino)ethanethiolate molecules and Re^{III}, determines the chemical properties of this series. The preference of this configuration over the six-co-ordinate $Re^{III}P_3S_3$ one, reported for other bidentate phosphinethiolate ligands, is based on spatial and electronic characteristics of this particular ligand. The fifth co-ordination site can accommodate a variety of monodentate thiolate ligands, differing in nucleophilicity and size. The X-ray structural data for compound **5** correlate well with those from other Re^{III} five-co-ordinate complexes, which contain the S_3 and two π back-bonding atom set.

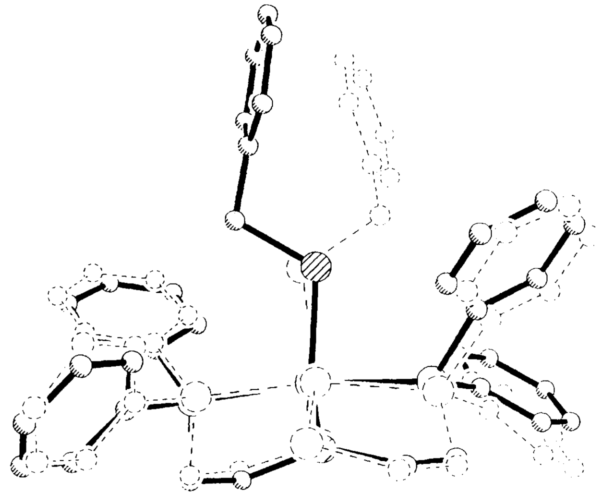


Fig. 2 Superimposition of molecule A (——) and B (– – –)

Experimental

All chemicals were of reagent grade and were used as such without further purification. Rhenium was purchased from Aldrich as $KReO_4$. Solvents were purged with nitrogen or argon before use. The syntheses were conducted under a nitrogen or argon inert atmosphere.

Elemental analyses for C, H and N were performed on an

Table 4 Comparison of the distances (Å) and angles (°) of ligands in mononuclear rhenium(III) complexes with co-ordination number 5, containing sulfur and phosphorus donor atoms

Complex	Co-ordinating set	Equatorial plane	Re–S	Re–P	S–Re–S(N)	P–Re–P(N)	Ref.
$[Re(SPh)_3(PPh_3)(MeCN)]$	S_3PN	S_3	2.255(6)	2.351(6)	120.0(3)	Not reported	10
$[Re(SC_6H_2Pr^i_3\text{-}2,4,6)_3(PPh_3)(N_2)]$	S_3PN	S_3	2.252(3)	2.386(3)	119.6(9)	178.2(3)	12
$[Re(SC_6H_4SiMe_3\text{-}o)(PPh_3)_2\text{-}\{NC(SC_6H_4SiMe_3\text{-}o)Me\}_2]$	SP_2N_2	SN_2	2.323(2)	2.421(2)	116.5(3)	169.6(1)	20
$[Re(Ph_2PCH_2CH_2S)_2(PhCH_2S)]$	S_3P_2	S_3	2.253(4)	2.368(4)	119.8(2)	170.5(1)	This work

automatic Perkin-Elmer 2400 elemental analyser. Analyses for S and Cl were obtained after decomposition in a Schöniger flask and subsequent titration of the sulfates and chlorides obtained by addition of $Ba(ClO_4)_2$ and $Hg(ClO_4)_2$, respectively. Phosphorus analyses were obtained by gravimetric determination [after decomposition with a sulfuric–nitric acid mixture and weighing the yellow precipitate formed by addition of $(NH_4)_3PO_4{\cdot}12MoO_3$].

IR spectra were recorded on a Perkin-Elmer 1760 spectrophotometer on KBr pellets in the region 4000–450 cm^{-1}. Proton and ^{31}P NMR spectra were recorded on a Bruker AC 200 spectrometer using various deuteriated solvents, with tetramethylsilane and 85% H_3PO_4, respectively, as internal standards. UV/VIS spectra were recorded on a Perkin-Elmer Lambda 15 spectrophotometer and mass spectra on a VG-ZAB2F double-focus instrument in positive FAB conditions. A 3-nitrobenzyl alcohol matrix was used and the ion gun operated at 8 keV (*ca.* 1.28 × 10^{-15} J) with xenon as the primary gas.

2-(Diphenylphosphino)ethanethiol was prepared by Argus Chemicals according to the literature method.[21] The product was distilled before use and the fraction distilled at 0.4 torr (*ca.* 53.2 Pa), 180–190 °C, was collected and stored under nitrogen. The synthesis of $[Re^VOCl_3(PPh_3)_2]$ **1** also followed a reported procedure[22] and the product (78%) was collected as yellow prismatic crystals. Reduction of complex **1** using PPh_3 in MeCN–toluene[23] gave $[Re^{III}Cl_3(MeCN)(PPh_3)_2]$ **2** (90%) as a yellow-orange crystalline solid.

Synthesis of the Complexes.—*Bis*[2-(*diphenylphosphino*)*ethanethiolato*-κS,κP][2-(*diphenylphosphino*)*ethanethiolato*-κS]*rhenium*(III) **3**. To toluene (10 cm^3)–EtOH (40 cm^3) degassed with argon were added complex **2** (200 mg, 0.23 mmol) and excess of $Ph_2PCH_2CH_2SH$ (1:4) (229.3 mg, 0.93 mmol). The orange suspension formed was refluxed with stirring under an argon atmosphere for 5 h. The resulting dark brown suspension was reduced to two-thirds of its volume by argon flux and left under argon overnight. A dark brown solid precipitated and was filtered with suction, rinsed with EtOH and Et_2O and dried under vacuum (150.6 mg). The solid was soluble in $CHCl_3$, CH_2Cl_2, toluene and benzene, slightly soluble in Me_2CO and MeCN and insoluble in H_2O, MeOH, EtOH, Et_2O and pentane. Brown crystals were obtained by slow evaporation of a CH_2Cl_2–MeCN solution. Yield 70% (Found: C, 54.0; H, 4.6; P, 9.8; S, 10.8. Calc. for $C_{42}H_{42}P_3ReS_3$: C, 54.7; H, 4.6; P, 10.1; S, 10.4%).

Bis[2-(*diphenylphosphino*)*ethanethiolato*-κS,κP][2-(*diphenylphosphoryl*)*ethanethiolato*-κS]*rhenium*(III) **4**. This compound was formed as a by-product during the synthesis of complex **3** when the reaction conditions were not strictly anaerobic and/or an old sample of $Ph_2PCH_2CH_2SH$ (partly oxidized) was used. However, the most favourable yields were obtained as follows. To toluene (10 cm^3)–EtOH (40 cm^3) degassed with argon was added complex **2** (200 mg, 0.23 mmol). To the orange suspension formed an excess of Pr^nSH (1:5; 88.9 mg, 105.8 μl, 1.17 mmol) and an excess of $Ph_2PCH_2CH_2SH$ (1:3; 172 mg, 143.3 μl, 0.70 mmol) were added. The mixture was refluxed under nitrogen and stirred for 3 h, resulting in a red-brown solution. The solvent was totally removed by nitrogen flux while stirring and using a slight heat. The oily red-brown residue was redissolved in MeOH–Et_2O (1:1, 10 cm^3) and left at ambient temperature overnight. The red-brown crystals that precipitated were filtered with suction, rinsed with Et_2O and dried in vacuum (160.5 mg, 73%). The compound was soluble in $CHCl_3$, CH_2Cl_2, toluene and benzene, slightly soluble in Me_2CO and MeCN and insoluble in H_2O, MeOH, EtOH, Et_2O and pentane.

Bis[2-(*diphenylphosphino*)*ethanethiolato*-κS,κP](*phenylmethanethiolato*-κS)*rhenium*(III) **5**. Complex **2** (200mg, 0.23 mmol) was suspended in degassed toluene (10 cm^3)–EtOH (30 cm^3) and excess of $PhCH_2SH$ (1:5; 145 mg, 137 μl, 1.17 mmol) and excess of $Ph_2PCH_2CH_2SH$ (1:3; 172 mg, 143.3 μl, 0.70 mmol) added thereafter forming an orange suspension. This was refluxed while stirring under nitrogen for 12 h forming a red-brown solution. The solution was removed totally by a nitrogen stream and the oily red-brown residue redissolved in a minimum amount of Et_2O. After addition of MeOH the mixture was left at ambient temperature overnight, whereupon red-brown crystals precipitated. These were filtered with suction, rinsed with MeOH and dried under vacuum (122 mg, 65%) (Found: C, 52.1; H, 4.5; P, 7.7; S, 11.9. Calc. for $C_{35}H_{35}P_2ReS_3$: C, 52.5; H, 4.4; P, 7.7; S, 12.0%). The crystalline solid was soluble in $CHCl_3$, CH_2Cl_2, toluene and benzene, slightly soluble in Me_2CO, MeCN and Et_2O and insoluble in H_2O, MeOH, EtOH and pentane. Crystals suitable for X-ray structural analysis were obtained by slow evaporation of a CH_2Cl_2–MeCN solution.

Bis[2-(*diphenylphosphino*)*ethanethiolato*-κS,κP](*benzenethiolato*-κS]*rhenium*(III) **6**. Complex **2** (200 mg, 0.23 mmol) was added to degassed toluene (10 cm^3)–EtOH (30 cm^3), followed by excess of PhSH (1:5; 129.2 mg, 143 μl, 1.17 mmol) and excess of $Ph_2PCH_2CH_2SH$ (1:3; 172 mg, 143.3 μl, 0.70 mmol). The orange suspension formed was refluxed under nitrogen while stirring for 5 h, gradually producing a red-brown solution. After expelling all the solvent using a nitrogen stream, the oily red-brown residue was redissolved in Et_2O–MeOH and left at room temperature overnight. The resulting green-grey precipitate was filtered by suction, rinsed with MeOH and dried in vacuum (130 mg). The solid was recrystallized from CH_2Cl_2–MeCN. Yield 71% (Found: C, 52.4; H, 4.2; P, 7.8; S, 11.1. Calc. for $C_{34}H_{33}P_2ReS_3$: C, 52.0; H, 4.2; P, 7.9; S, 12.2%). The compound was soluble in $CHCl_3$, CH_2Cl_2, Et_2O, slightly soluble in MeOH, EtOH and MeCN and insoluble in H_2O and pentane.

Bis[2-(*diphenylphosphino*)*ethanethiolato*-κS,κP](*propanethiolato*-κS)*rhenium*(III) **7**. Complex **2** (200 mg, 0.23 mmol) was suspended in degassed (argon flux) benzene (10 cm^3)–MeOH (30 cm^3) and excess of Pr^nSH (1:5; 88.9 mg, 105.8 μl, 1.17 mmol) and excess of $Ph_2PCH_2CH_2SH$ (1:3; 172 mg, 143.3 μl, 0.70 mmol) were added. This mixture was refluxed while stirring in an argon atmosphere for 4 h, gradually resulting in a red-brown solution. The latter was reduced to two-thirds of its volume by an argon stream, whereupon a dark brown solid precipitated. This was filtered under argon pressure, washed with degassed MeOH and finally dried in a vacuum (142 mg, 81%). The solid was soluble in $CHCl_3$, CH_2Cl_2 and Et_2O,

Table 5 Structure determination summary

Crystal data	
Empirical formula	$C_{35}H_{35}P_2ReS_3$
Crystal dimensions/mm	0.24 × 0.24 × 0.30
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	21.011(9)
b/Å	20.397(9)
c/Å	16.289(7)
β/°	107.13(5)
U/Å^3	6671.2
Z	8
D_c/Mg m^{-3}	1.59
μ/mm^{-1}	3.9
F(000)	3184
Data collection	
Diffractometer	Siemens R3m/V
Radiation	Mo-Kα (λ = 0.710 73 Å)
T/K	294
Monochromator	Highly oriented graphite crystal
2θ range/°	4.0–45.0
Scan type, speed (° min^{-1}), range (°)	ω, variable (3–15), 1.20
Index ranges	$-21 \leqslant h \leqslant 21, 0 \leqslant k \leqslant 22, 0 \leqslant l \leqslant 17$
Reflections collected	9310
Independent reflections	8648
Observed reflections [$F_o > 4\sigma(F_o)$]	5644
Absorption correction	Empirical; ψ-scan method for four reflections at *ca.* $\chi = 90°$; $0.63 <$ transmission factor < 1.00
Solution and refinement	
System used	Siemens SHELXTL-PLUS[24]
Solution	Heavy-atom methods
Refinement method	Full-matrix least-squares
Quantity minimized	$\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2$
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.0097F^2$
Thermal parameters	Heavy atoms + carbon atoms nearest to co-ordination sphere, anisotropic
Final R, R' (obs. data)	0.050, 0.063
Goodness-of-fit	0.62
Data-to-parameter ratio	12.8:1
Largest difference peak/e Å^{-3}	1.43 [1.05 Å from Re(1)]
Largest difference hole/e Å^{-3}	−0.65

slightly soluble in MeOH and EtOH and insoluble in H_2O and *n*-pentane. Because of oxidation/decomposition of the product during recrystallization, it was not possible to isolate this compound in a form satisfactorily pure to conduct an elemental analysis.

Crystallography.—A dark green rhomboid of complex **5**, grown as described above, was used for the data collection. Details of the crystal data, intensity measurements and data processing are summarized in Table 5. Hydrogen atoms were introduced at the expected positions with a common U value of 0.09 Å^2, but they were not refined.

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

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