# Synthesis, structure and reactivity of tetranuclear square-type complexes of rhenium and manganese bearing pyrimidine-2-thiolate (pymS) ligands: versatile and efficient precursors for mono- and polynuclear compounds containing $M(CO)_3$ (M = Re, Mn) fragments<sup>†</sup>

S. E. Kabir,\*<sup>*a*</sup> J. Alam,<sup>*a*</sup> S. Ghosh,<sup>*a*</sup> K. Kundu,<sup>*a*</sup> G. Hogarth,\*<sup>*b*</sup> D. A. Tocher,<sup>*b*</sup> G. M. G. Hossain<sup>*c*</sup> and H. W. Roesky\*<sup>*d*</sup>

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Reactions of  $M_2(CO)_{10}$  (M = Re, Mn) with pyrimidine-2-thiol (pymSH) in the presence of Me<sub>3</sub>NO afford the tetranuclear square-type complexes  $[M_4(CO)_{1/2}(\mu - \kappa^3 - pymS)_4]$  (1, M = Re; 2, M = Mn). Both consist of four  $M(CO)_3$  (M = Re, Mn) units, pairs of which are joined by tridentate pyrimidine-2thiolate ligands. Treatment of 1-2 with a variety of donor ligands results in cleavage of the square to afford mononuclear species with either a mono- or bidentate pyrimidine-2-thiolate ligand. Triphenylphosphine reacts with 2 to give  $[Mn(CO)_3(PPh_3)(\kappa^2-pymS)]$  (3) in which the pyrimidine-2thiolate coordinates in a bidentate fashion. With diamines  $[M(CO)_3(\kappa^2-L)(\kappa^1-pymS)]$  (4–7) (M = Re. Mn; L = 2.2'- bipy, 1,10-phen, en) result in which the pyrimidine-2-thiolate binds in a monodentate fashion through sulfur. With diphosphines, complexes with different stoichiometries and pyrimidine-2-thiolate binding modes are obtained depending on the nature of the metal and diphosphine. With dppm and dppe, 1 gives  $[Re(CO)_2(\kappa^1-pymS)(\kappa^2-dppm)]$  (8) and  $[Re(CO)_2(\kappa^2-dppm)]$ pymS)( $\kappa^1$ -dppe)<sub>2</sub>] (10), respectively, whereas 2 affords [Mn(CO)<sub>2</sub>( $\kappa^2$ -pymS)( $\kappa^1$ -dppm)<sub>2</sub>] (9) and  $[Mn(CO)_2(\kappa^2-pyS)(\kappa^2-dppe)]$  (11) under similar conditions. Reactions of 1–2 with  $[Os_3(CO)_{10}(NCMe)_2]$ affords mixed-metal butterfly clusters  $[MOs_3(CO)_{13}(\mu_3-\kappa^2-pymS)]$  (12–13) in which the group 7 metal occupies a wing-tip position and the pyrimidine-2-thiolate ligand caps a triangular Os<sub>2</sub>M face. With  $Ru_3(CO)_{12}$ , carbon–sulfur bond cleavage occurs to give the tetranuclear clusters  $[MRu_3(CO)_{14}(\mu_4-S)(\mu_5)(\mu_5-S)(\mu_5-S)(\mu_5-S))]$  $\kappa^{1}$ : $\eta^{1}$ -pym)] (14–15) bearing both the extruded sulfur and the heterocyclic ring. The molecular structures of 1-7, 10 and 12 have been established by X-ray diffraction allowing the binding mode of the pyrimidine-2-thiolate ligands to be probed.

# Introduction

Over the past two decades self-assembly phenomena have been utilised for the construction of highly organised metal-containing macrocycles, becoming an attractive and fruitful pathway for macrocyclisation, since the usual synthetic routes for the cyclisation of large molecules are frequently tedious and lowyielding.<sup>1-4</sup> Molecular square-type complexes are amongst the most widely studied of this family of macrocycles, their synthesis being pioneered by Stang,<sup>5-9</sup> Fujita<sup>10-14</sup> and their co-workers. While over the past twenty years, a large number of square-type complexes have been prepared, the vast majority are based on a square-planar metal coordination geometry, and in contrast those based on the more common octahedral metal building blocks are relatively rare.<sup>15-25</sup> This seems somewhat unexpected and indeed the first square-type complexes reported by Verkade and co-workers contained the octahedral  $M(CO)_4$  (M = Cr, W) linking units.<sup>15</sup> More recently, Hupp and co-workers have linked Re(CO)<sub>3</sub>Cl units together with 4,4'-bipy and related ligands<sup>16</sup> and Lees have made a series of related group 7 square-like complexes.<sup>17-19</sup>

Pyrimidine-2-thiolate is a versatile ligand known to exhibit a variety of coordination geometries (Chart 1) and mono-, di- and polynuclear metal complexes containing this ligand have been shown to display a range of different structural types.<sup>26</sup> Reactions



<sup>&</sup>lt;sup>a</sup>Department of Chemistry, Jahangirnagar University, Savar, Dhaka 1342, Bangladesh

<sup>&</sup>lt;sup>b</sup>Department of Chemistry, University College London, 20 Gordon Street, London, UK WC1H0AJ

<sup>&</sup>lt;sup>c</sup>Department of Chemistry, Dhaka University, Dhaka 1000, Bangladesh

<sup>&</sup>lt;sup>d</sup>Institute of Inorganic Chemistry, Georg-August University of Göttingen, Tammannstr. 4, 37077 Göttingen, Germany

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of  $M_2(CO)_{10}$  (M = Re, Mn) with pyridine-2-thiol in the presence of  $Me_3NO$  afford dinuclear complexes  $[M_2(CO)_6(\mu-pyS)_2]$ , containing two pyridine-2-thiolate ligands, each acting as a five-electron donor through coordination of both sulfur and nitrogen atoms.<sup>27,28</sup> Pyrimidine-2-thiolate contains an extra nitrogen coordination site and should be capable of binding concurrently to a number of different atoms. This was appealing to us in our attempts to develop systematic syntheses of multimetallic clusters and herein we report the synthesis, structure and reactivity of *fac*-tricarbonyl manganese(I)- and rhenium(I)-based self-assembled square-type complexes containing pyrimidine-2-thiolate as the bridging ligand.

### **Results and discussion**

### (a) Synthesis and structure of tetranuclear square-type complexes

Reaction of  $M_2(CO)_{10}$  (M = Re, Mn) with pyrimidine-2-thiol in presence of Me<sub>3</sub>NO at 25 °C affords the tetranuclear complexes  $[M_4(CO)_{12}(\mu-\kappa^3-pymS)_4]$  (1, M = Re, 68%; 2, M = Mn, 72%). In each, the pyrimidine-2-thiolate ligands act as five electron donors binding through sulfur and both nitrogen atoms (Scheme 1). Both 1 and 2 have been characterised by a combination of spectroscopic data and single-crystal X-ray crystallography. Each shows two strong carbonyl absorptions in the IR spectra, and <sup>1</sup>H NMR spectra are consistent with the presence of single type of pyrimidine-2-thiolate ligand. However, on this basis the stoichiometry of the complexes could not be determined. In the FAB mass spectra, peaks at m/z 1526 for 1 and m/z 1000 for 2 were suggestive of tetranuclear clusters. However, the precise attachment of the ligands could only be obtained by X-ray diffraction studies, the results of which are summarised in Fig. 1 and 2.



The solid-state structures show that the molecules are indeed tetranuclear; the four separate metal tricarbonyl units are joined by pyrimidine-2-thiolate ligands. These bridge *via* coordination of a single nitrogen atom to one metal atom and a chelating interaction to another *via* the second nitrogen and sulfur atom. The result is an overall square-like arrangement. The overall coordination geometry of each metal is best described as a distorted octahedron with a *cis*-arrangement of the pyrimidine-2-thiolate ligands. Each metal is bound to three facially arranged carbonyls, the average metal–carbon distance (1.903(14) Å in 1; 1.803(3) Å in 2) being similar to those observed in related complexes.<sup>27-33</sup> Two of the pyrimidine-2-thiolate ligands lie above and two below the M<sub>4</sub> plane, being slightly tilted with respect to one another. The M–N<sub>bri</sub> distances (av. 2.231(9) Å in 1; av. 2.109(2) Å in 2) are somewhat longer than the M–N<sub>che</sub> distances



Fig. 1 ORTEP diagram of the molecular structure of  $[Re_4(CO)_{12}(\mu-\kappa^3-pymS)_4]$  (1), showing 50% probability thermal ellipsoids. Selected interatomic distances (Å) and angles (°): Re(1)–N(1) 2.175(9), Re(1)–N(8) 2.217(9), Re(2)–N(3) 2.179(9), Re(2)–N(2) 2.246(9), Re(3)–N(5) 2.180(9), Re(3)–N(4) 2.220(9), Re(4)–N(7) 2.177(8), Re(4)–N(6) 2.239(9), Re(1)–S(1) 2.539(3), Re(2)–S(2) 2.533(3), Re(3)–S(3) 2.518(3), Re(4)–S(4) 2.545(3), av. C–S 1.706(11), av. Re–C 1.903(14), N(1)–Re(1)–N(8) 86.4(3), N(8)–Re(1)–S(1) 83.6(2), N(1)–Re(1)–S(1) 65.1(2), N(3)–Re(2)–N(2) 86.9(3), N(3)–Re(2)–S(2) 65.0(2), N(2)–Re(2)–S(2) 83.6(2), N(5)–Re(3)–N(4) 86.7(3), N(4)–Re(3)–S(3) 84.7(2), N(5)–Re(3)–S(3) 64.7(2), N(7)–Re(4)–N(6) 86.0(3), N(7)–Re(4)–S(4) 64.8(2), N(6)–Re(4)–S(4) 82.7(2).



**Fig. 2** ORTEP diagram of the molecular structure of  $[Mn_4(CO)_{12}(\mu-\kappa^3-pymS)_4]$  (**2**), showing 50% probability thermal ellipsoids. Selected interatomic distances (Å) and angles (°): Mn(1)–N(1) 2.037(2), Mn(1)–N(8) 2.101(2), Mn(2)–N(3) 2.056(3), Mn(2)–N(2) 2.109(2), Mn(3)–N(5) 2.034(3), Mn(3)–N(4) 2.123(2), Mn(4)–N(7) 2.022(2), Mn(4)–N(6) 2.101(3), Mn(1)–S(1) 2.4130(9), Mn(2)–S(2) 2.4032(9), Mn(3)–S(3) 2.4232(9), Mn(4)–S(4) 2.4370(9), av. C–S 1.714(3), av. Mn–C 1.803(3), N(1)–Mn(1)–N(8) 87.52(9), N(8)–Mn(1)–S(1) 87.00(7), N(1)–Mn(1)–S(1) 68.71(7), N(3)–Mn(2)–N(2) 87.80(10), N(3)–Mn(2)–S(2) 68.52(7), N(2)–Mn(2)–S(2) 86.69(7), N(5)–Mn(3)–N(4) 87.68(10), N(4)–Mn(3)–S(3) 86.61(7), N(5)–Mn(3)–S(3) 68.39(8), N(7)–Mn(4)–N(6) 86.78(10), N(7)–Mn(4)–S(4) 68.53(7), N(6)–Mn(4)–S(4) 86.34(7).

(2.178(9) Å in 1; 2.037(2) Å in 2) but both being within the range reported for related compounds.<sup>27-36</sup> The average N–M–S chelate angles (64.9(2)° in 1; 68.54(7)° in 2) are similar to those found in related dinuclear complexes [Re<sub>2</sub>(CO)<sub>6</sub>( $\mu$ -MepyS)<sub>2</sub>]<sup>27</sup>

(av. 65.7(3)°) and  $[Mn_2(CO)_6(\mu-pyS)_2]^{28}$  (av. 69.27(8)°) and the average M-S distances (2.534(3) Å in 1; 2.4191(9) Å in 2) are in agreement with those in the literature.<sup>27,28,33,36-38</sup> The diagonal M-M contacts are 8.1768(17) and 8.309(3) Å in 1 and 7.8688(10) and 7.9362(10) Å in 2. Each pyrimidine-2-thiolate ligand serves as five-electron donor and hence each metal achieves an 18-electron configuration without any metal-metal interaction. To the best of our knowledge, the tetranuclear square-type skeletal geometry of 1 and 2 containing heterocyclic ligands and fac-M(CO)<sub>3</sub> fragments has not previously been detailed.

# (b) Reactivity of 1 and 2 toward various mono- and bidentate ligands

Treatment of either 1 or 2 with various mono- and bidentate group 15 ligands resulted in breakdown of the square to give mononuclear species within which the coordination geometry of the pyrimidine-2-thiolate ligand varies. Reaction of 2 with PPh<sub>3</sub> gives mononuclear  $[Mn(CO)_3(PPh_3)(\kappa^2-pymS)]$  (3) in 55% yield (Scheme 2). Now three strong carbonyl absorptions are seen in the IR spectrum and the  ${}^{31}P{}^{1}H$  NMR shows a simple singlet at  $\delta$  58.3 ppm. An ORTEP diagram of the molecular structure of 3 is depicted in Fig. 3, and selected bond lengths and angles are listed in the caption. The molecule contains a single manganese atom with three carbonyl groups, a triphenylphosphine ligand and a chelating pyrimidine-2-thiolate ligand. The coordination geometry around the manganese atom is a distorted octahedron with three carbonyl groups arranged in a facial fashion. The distortion from octahedral coordination geometry is evident from the short N–Mn–S chelate angle  $(68.73(4)^{\circ})$  of the heterocyclic ligand which is similar to that observed in 2. The best equatorial plane is defined by the nitrogen and sulfur atoms of the chelating ligands and the carbon atoms of two carbonyl groups (C(1) and C(2)). The triphenylphosphine ligand occupies an axial site with







Fig. 3 ORTEP diagram of the molecular structure of [Mn(CO)<sub>3</sub>-(PPh<sub>3</sub>)( $\kappa^2$ -pymS)] (3), showing 35% probability thermal ellipsoids. Selected interatomic distances (Å) and angles (°): Mn(1)-C(1) 1.7993(19), Mn(1)-C(2) 1.8027(18), Mn(1)-C(3) 1.8291(19), Mn(1)-N(1) 2.0376(15), Mn(1)-P(1) 2.3612(5), Mn(1)-S(1) 2.4133(5), C(4)-S(1) 1.7237(17), C(1)-Mn(1)-C(2) 94.72(8), C(1)-Mn(1)-C(3) 86.12(8), N(1)-Mn(1)-S(1) 68.73(4), C(2)-Mn(1)-C(3) 90.58(8), P(1)-Mn(1)-C(3) C(2)-Mn(1)-N(1) 98.66(7), C(1)-Mn(1)-S(1) 97.95(6), C(4)-S(1)-Mn(1) 78.89(6).

respect to this plane and the manganese-phosphorus distance is somewhat larger than those normally found in the literature.<sup>39</sup> Other bond distances are similar to those found in 2.

Reactions of 1 with 2,2'-bipyridine (bipy) and 1,10-phenanthroline (phen) afford [Re(CO)<sub>3</sub>( $\kappa^2$ -bipy)( $\kappa^1$ -pymS)] (4) and [Re- $(CO)_3(\kappa^2-phen)(\kappa^1-pymS)$ ] (5) in 62 and 66% yields, respectively. Similarly, upon treatment with phen or ethylenediamine (en) 2 gives  $[Mn(CO)_3(\kappa^2-phen)(\kappa^1-pymS)]$  (6) and  $[Mn(CO)_3(\kappa^2-en)(\kappa^1-\kappa^2-en)(\kappa^2-en)$ pymS)] (7) in 62 and 68% yields (Scheme 2). The IR spectra all show three carbonyl bands indicative of a fac-M(CO)<sub>3</sub> centre. NMR spectra are generally not particularly informative; in addition to aromatic resonances the <sup>1</sup>H NMR spectrum of 7 shows two multiplets at  $\delta$  4.92 and 2.95 ppm assigned to the amine and methylene protons, respectively, of the ethylenediamine ligand. The mass spectrum of all of them exhibits the parent molecular ion peak and peaks due to stepwise loss of three carbonyls. The molecular structures of 4-7 are shown in Fig. 4-7. All have the same overall structure consisting of a single metal atom with three carbonyl groups arranged in a facial fashion, a chelating diamine ligand and monodentate pyrimidine-2-thiolate ligand. The metal atom is a distorted octahedron, the main distortion being due to the small bite-angle of the bidentate ligand  $(74.4(1)^{\circ})$ in 4; 75.5(2)  $^{\circ}$  in 5; 79.19(7) $^{\circ}$  in 6; and 80.95(7) $^{\circ}$  in 7). In all, the donor atoms of the bidentate ligand and the carbons of two of the carbonyls constitute the best equatorial plane around the metal centre with only small deviations from planarity and the metal atom is practically in this plane. The M-C, M-N,



Fig. 4 ORTEP diagram of the molecular structure of  $[Re(CO)_3-(\kappa^2-bipy)(\kappa^1-pymS)]$  (4), showing 50% probability thermal ellipsoids. Selected interatomic distances (Å) and angles (°): Re(1)–C(1) 1.914(5), Re(1)–C(2) 1.914(5), Re(1)–C(3) 1.927(5), Re(1)–N(1) 2.182(4), Re(1)–N(2) 2.167(4), Re(1)–S(1) 2.5012(13), C(14)–S(1) 1.739(5), C(3)–Re(1)–S(1) 178.52(15), N(2)–Re(1)–N(1) 74.43(14), N(2)–Re(1)–S(1) 86.10(10), N(1)–Re(1)–S(1) 80.46(11), C(14)–S(1)–Re(1) 110.32(16), C(2)–Re(1)–C(1) 88.4(2), C(2)–Re(1)–N(1) 97.78(18), C(2)–Re(1)–N(2) 172.12(18).



Fig. 5 ORTEP diagram of the molecular structure of  $[Re(CO)_{3}-(\kappa^{2}-phen)(\kappa^{1}-pymS)]$  (5), showing 50% probability thermal ellipsoids. Selected interatomic distances (Å) and angles (°): Re(1)–C(1) 1.916(8), Re(1)–C(2) 1.900(8), Re(1)–C(3) 1.899(10), Re(1)–N(1) 2.182(6), Re(1)–N(2) 2.171(5), Re(1)–S(1) 2.506(2), C(16)–S(1) 1.753(8), C(3)–Re(1)–S(1) 174.3(2), N(2)–Re(1)–N(1) 75.5(2), N(2)–Re(1)–S(1) 86.29(17), N(1)–Re(1)–S(1) 84.48(17), C(16)–S(1)–Re(1) 110.6(3), C(2)–Re(1)–C(1) 90.3(3), C(2)–Re(1)–N(1) 98.7(3), C(2)–Re(1)–N(2) 171.6(3).

and M-S distances are similar to those observed in the parent complexes.

In contrast to the behaviour with diamines, reactions of **1** and **2** with diphosphines give different products depending on both the backbone of the diphosphine and the size of the metal. Reaction of **1** with bis(diphenylphosphino)methane (dppm) affords [Re(CO)<sub>2</sub>( $\kappa^2$ -dppm)( $\kappa^1$ -pymS)] (**8**) in 42% yield, which is structurally akin to the diamine complexes. The IR spectrum shows three strong carbonyl absorption bands and in the <sup>1</sup>H NMR spectrum, in addition to the aromatic resonances, two equal intensity multiplets at  $\delta$  3.28 and 3.76 ppm were observed. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum exhibits two doublets at  $\delta$  13.7 and 23.4 ppm ( $J_{PP} = 88.4$  Hz) indicating the expected non-equivalence



Fig. 6 ORTEP diagram of the molecular structure of  $[Mn(CO)_3-(\kappa^2-phen)(\kappa^1-pymS)]$  (6), showing 50% probability thermal ellipsoids. Selected interatomic distances (Å) and angles (°): Mn(1)–C(1) 1.800(3), Mn(1)–C(2) 1.806(3), Mn(1)–C(3) 1.801(2), Mn(1)–N(3) 2.0531(18), Mn(1)–N(4) 2.0556(17), Mn(1)–S(1) 2.3788(6), C(4)–S(1) 1.738(2), C(1)–Mn(1)–S(1) 174.07(8), N(3)–Mn(1)–N(4) 79.19(7), N(4)–Mn(1)–S(1) 86.11(5), N(3)–Mn(1)–S(1) 82.16(5), C(4)–S(1)–Mn(1) 113.61(7), C(3)–Mn(1)–C(2) 88.47(11), C(2)–Mn(1)–N(3) 97.41(9), C(2)–Mn(1)–N(4) 174.96(9).



Fig. 7 ORTEP diagram of the molecular structure of  $[Mn(CO)_3-(\kappa^2-en)(\kappa^1-pymS)]$  (7), showing 50% probability thermal ellipsoids. Selected interatomic distances (Å) and angles (°): Mn(1)-C(1) 1.786(2), Mn(1)-C(2) 1.798(2), Mn(1)-C(3) 1.800(2), Mn(1)-N(1) 2.0752(17), Mn(1)-N(2) 2.0828(17), Mn(1)-S(2) 2.4067(6), C(6)-S(2) 1.740(2), C(2)-Mn(1)-N(1) 92.01(9), C(1)-Mn(1)-N(2) 94.67(9), N(2)-Mn(1)-S(2) 86.94(5), N(1)-Mn(1)-N(2) 80.95(7), C(2)-Mn(1)-S(2) 176.74(8), N(1)-Mn(1)-S(2) 91.21(5), C(6)-S(2)-Mn(1) 114.51(7), C(1)-Mn(1)-C(3) 89.05(10), C(1)-Mn(1)-N(1) 175.59(9).

of the phosphorus atoms. In contrast, reaction of 2 with dppm gave the bis(diphosphine) complex  $[Mn(CO)_2(\kappa^2-pymS)(\kappa^1-dppm)_2]$  (9) in 26% yield (Scheme 2). This was characterised by a comparison of spectroscopic data with those of  $[Mn(CO)_2(\kappa^2-MepyS)(\kappa^1$ dppm)<sub>2</sub>]<sup>28a</sup> and [Mn(CO)<sub>2</sub>( $\kappa^2$ -pyS)( $\kappa^1$ -dppm)<sub>2</sub>].<sup>28b</sup> The IR spectrum shows two strong carbonyl bands and the FAB mass spectrum gave a molecular ion at m/z 990. Most informative was the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum which displays a singlet at  $\delta$  64.8 ppm (broad and unresolved, coordinated P atom) and a sextet at  $\delta$  –23.8 ppm (J ca. 31.4 within each ligand, J ca. 56.7 Hz between two ligands and across the manganese atom, non-coordinated P atom) like  $[Mn(CO)_2(\kappa^2-MepyS)(\kappa^1-dppm)_2]$ .<sup>28</sup> The sextet consists of four closely spaced central lines of almost equal intensity and two outer lines of small intensity at comparatively large distance for the uncoordinated phosphorus atoms while the broad and unresolved resonance appeared due to the coordinated phosphorus atoms.<sup>28b</sup> The differing reactivity of 1 and 2 towards dppm is somewhat surprising but may reflect the stronger manganese–nitrogen *versus* rhenium–nitrogen interactions, and also the known propensity of the small bite-angle diphosphine to more readily form chelate complexes with the heavier (larger) transition metals.

Treatment of 1 with bis(diphenylphosphino)ethane (dppe) furnishes [Re(CO)<sub>2</sub>( $\kappa^2$ -pymS)( $\kappa^1$ -dppe)<sub>2</sub>] (10) in 30% yield, which is structurally analogous to 9. The IR spectrum exhibits two strong carbonyl bands, while the FAB mass spectrum shows a molecular ion at m/z 1150 together with peaks for successive loss of both carbonyls. In addition to the usual resonances for the phenyl and pyrimidyl protons, the <sup>1</sup>H NMR spectrum shows four equal intensity multiplets at  $\delta$  2.10, 2.30, 2.50, and 3.05 ppm for the methylene protons of the diphosphine ligands, while the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum displays two singlets at  $\delta$  35.0 and 47.6 ppm. The molecular structure of 10 was confirmed by an X-ray crystallographic study, the results of which are summarised in Fig. 8. The molecule contains a single rhenium atom with two carbonyl ligands, two monodentate dppe ligands and a chelating pyrimidine-2-thiolate ligand, the latter being bonded to rhenium through the sulfur and one nitrogen atom. The coordination geometry at the rhenium atom is a highly distorted octahedron, the small chelate angle of the pyrimidine-2-thiolate ligand (65.20(14)°) being similar to that in 1. The molecule contains a crystallographic plane of symmetry containing the two carbonyls and pyrimidine-2-thiolate ligand and the pendent diphosphine ligands lie trans to one another, presumably to minimise steric congestion. The Re–P bond length, Re(1)–P(1), of 2.3988(9) Å is within the range found in the literature<sup>30,40,41</sup> while other bond distances are similar to those observed in 1. The reaction of dppe with 2 again differs from that of 1 affording  $[Mn(CO)_2(\kappa^2-pymS)(\kappa^2-dppe)]$  (11) in 38% yield (Scheme 2). The IR spectrum exhibits carbonyl bands at 1937 and 1858 cm<sup>-1</sup>, while the FAB mass spectrum shows a molecular ion at m/z 620. In the <sup>1</sup>H NMR spectrum, in addition to the aromatic resonances, a series of multiplets between  $\delta$  2.01– 3.36 ppm are assigned to the methylene protons of the diphosphine ligand, while the  ${}^{31}P{}^{1}H$  NMR spectrum shows two singlets at

 $\begin{array}{c} P^2 \\ P^2 \\ C^2 \\ P^2 \\ C^2 \\ C^2 \\ Re1 \\ C^3 \\ C^3 \\ C^4 \\$ 

**Fig. 8** ORTEP diagram of the molecular structure of  $[\text{Re}(\text{CO})_2-(\kappa^2-\text{pymS})(\kappa^1-\text{dppe})_2]$  (**10**), showing 35% probability thermal ellipsoids. Selected interatomic distances (Å) and angles (°): Re(1)–C(1) 1.894(6), Re(1)–C(2) 1.895(7), Re(1)–N(1) 2.172(5), Re(1)–P(1) 2.3988(9), Re(1)–P(1') 2.3988(9), Re(1)–S(1) 2.5426(15), C(3)–S(1) 1.743(7), C(1)–Re(1)–C(2) 93.1(3), P(1)–Re(1)–P(1') 176.25(5), N(1)–Re(1)–S(1) 65.20(14), P(1')–Re(1)–S(1) 88.93(2), C(3)–S(1)–Re(1) 80.75(19), C(1)–Re(1)–N(1) 100.4(2), C(2)–Re(1)–N(1) 166.5(2), C(1)–Re(1)–P(1') 90.66(2), C(1)–Re(1)–P(1') 90.66(2).

 $\delta$  98.9 and 77.6 ppm due to the non-equivalent phosphorus nuclei. These data are similar to those found for the related manganese complex [Mn(CO)<sub>2</sub>( $\kappa^2$ -S<sub>2</sub>NC<sub>7</sub>H<sub>4</sub>)( $\kappa^2$ -dppe)].<sup>42</sup>

# (c) Formation of mixed-metal clusters

We recently reported the synthesis of a series of mixed-metal clusters  $[MM'_3(CO)_{13}(\mu-SN_2C_4H_5)]$  (M = Mn, Re; M' = Ru, Os) obtained from reactions between  $[M_2(CO)_6(\mu-SN_2C_4H_5)_2]$  and  $[M'_3(CO)_{10}L_2]$  (L = CO, MeCN). In these, the facile metal–sulfur bond cleavage of dimeric  $[M_2(CO)_6(\mu-N_2C_4H_5)_2]$  is believed to generate reactive mononuclear intermediates,  $[M(CO)_{10}(NCMe)_2]$  and  $Ru_3(CO)_{12}$ .<sup>43</sup> In an attempt to prepare further tetranuclear mixed-metal clusters of this type, we have investigated the reactions of 1 and 2 with  $[Os_3(CO)_{10}(NCMe)_2]$  and  $Ru_3(CO)_{12}$ . Reactions of 1 and 2 with  $[Os_3(CO)_{10}(NCMe)_2]$  in refluxing benzene afforded the mixed-metal clusters  $[ReOs_3(CO)_{13}(\mu_3-\kappa^2-pymS)]$  (12) and  $[MnOs_3(CO)_{13}(\mu_3-\kappa^2-pymS)]$  (13) in 40 and 31% yields, respectively (Scheme 3).



The molecular structure of **12** is depicted in Fig. 9, and selected bond angles and distances are listed in the caption. The cluster consists of four metal atoms in a butterfly array with the rhenium atom occupying a wing-tip position. The triply bridging



Fig. 9 ORTEP diagram of the molecular structure of  $[ReOs_3(CO)_{13}-(\mu_3-\kappa^2-pymS)]$  (12), showing 50% probability thermal ellipsoids. Selected interatomic distances (Å) and angles (°): Os(1)–Os(2) 2.8626(8), Os(1)–Os(3) 2.8685(8), Os(2)–Os(3) 2.7896(8), Os(2)–Re(4) 2.9310(9), Os(3)–Re(4) 2.9107(9), Os(2)–S(1) 2.419(4), Os(3)–S(1) 2.411(4), Re(4)–N(1) 2.212(11), C(14)–S(1) 1.781(14), Os(2)–Os(1)–Os(3) 58.256(19), Os(3)–Os(2)–Os(1) 60.98(2), Os(2)–Os(3)–Os(1) 60.77(2), Os(3)–Os(2)–Re(4) 61.11(2), Os(1)–Os(2)–Re(4) 118.03(3), Os(2)–Os(3)–Re(4) 61.84(2), Os(1)–Os(3)–Re(4) 118.51(3), Os(3)–Re(4)–Os(2) 57.048(19), Os(3)–S(1)–Os(2) 70.55(10).

pyrimidine-2-thiolate ligand is facially located on the convex side of the cluster which bridges the hinge metal atoms through the sulfur atom, but coordinates to the wing-tip rhenium atom through a nitrogen atom. The cluster has thirteen terminal carbonyl groups, three of which are bonded to each of the hinge metal and the wingtip rhenium, while four are bonded to the wing-tip osmium. The average metal-metal distance in 12 (2.8725(9) Å) is similar to that of the 2-mercapto-1-methylimidazolate complex  $[ReOs_3(CO)_{13}(\mu_3 \kappa^2$ -SN<sub>2</sub>C<sub>4</sub>H<sub>5</sub>]<sup>43</sup> (2.8762(4) Å). The molecule contains a noncrystallographic mirror plane of symmetry passing through the plane of the heterocyclic ring and also containing the wing-tip metals of the butterfly. Assuming that the pyrimidine-2-thiolate ligand serves as a five electron donor, then 12 is electronically saturated with a total electron count of 62. The solid-state structure of 12 is supported by the solution spectroscopic data. The <sup>1</sup>H NMR spectrum displays a triplet at  $\delta$  7.31 ppm (J = 5.6 Hz) and two doublets of doublets at  $\delta$  8.80 ppm (J = 2.4, 5.6 Hz) and 9.66 ppm (J = 2.4, 5.6 Hz) assigned to the ring protons of the pyrimidine-2-thiolate ligands. The infrared spectrum of 12 is similar to that of  $[\text{ReOs}_3(\text{CO})_{13}(\mu_3-\kappa^2-\text{SN}_2\text{C}_4\text{H}_5)]^{43}$  while the FAB mass spectrum shows a molecular ion at m/z 1234. In view of the similarity of the IR spectra of 13 to those of 12,  $[ReOs_3(CO)_{13}(\mu_3-\kappa^2-SN_2C_4H_5)]^{43}$  and  $[MnOs_3(CO)_{13}(\mu_3-\kappa^2-\kappa^2-\kappa^2-\kappa^2)]^{43}$  $SN_2C_4H_5$ ],<sup>43</sup> it is reasonable to suggest that they are isostructural. The <sup>1</sup>H NMR spectrum of **13** displays three broad singlets in the aromatic region with a relative intensity of 1:1:1 and the FAB mass spectrum shows a molecular ion at m/z 1102 together with peaks due to sequential loss of all thirteen carbonyls.

Heating 1 and 2 with  $Ru_3(CO)_{12}$  affords the sulfido-bridged tetranuclear clusters [MRu<sub>3</sub>(CO)<sub>14</sub>( $\mu_4$ -S)( $\mu$ - $\kappa^1$ : $\eta^1$ -pym)] (14–15) in moderate yields. Both are characterised by comparison of their thpym)] (thpymH = tetrahydropyrimidine) which, on the basis of an X-ray diffraction study, consists of an Re(CO)<sub>3</sub>(thpym) moiety coupled with one  $Ru(CO)_4$  and two  $Ru(CO)_3$  units and is electron precise with two metal-metal bonds reported by Deeming et al. 44,45 The carbonyl regions of the IR spectra of 14 and 15 are very similar to that of [ReRu<sub>3</sub>(CO)<sub>14</sub>( $\mu_4$ -S)( $\mu$ - $\kappa^1$ : $\eta^1$ -thpym)] indicating that the three are isostructural. The <sup>1</sup>H NMR spectra of both display two sets of resonances in the aromatic region attributed to the presence of two isomers in solution relating to the relative positions of the pyrimidinate and group 7 carbonyl centres,44 and the FAB mass spectra show a parent molecular ion at 993 (14) and 863 (15) together with fragmentation peaks due to successive loss of fourteen carbonyl ligands which are consistent with our proposed structures. The cleavage of the carbon-sulfur bond at the ruthenium centre reflects the facile nature of the oxidative addition at this metal.

# Conclusions

Herein, we have documented the synthesis, structure, and reactivity of tetranuclear square-type complexes of rhenium and manganese. These macrocyclic supramolecules can be prepared, in a predictable way, by assembling suitable polydentate bridging ligand (*e.g.* pyrimidine-2-thiolate) and *fac*-M(CO)<sub>3</sub> corners. The self-assembly process possibly proceeds through the formation of the intermediate dimeric,  $[M_2(CO)_6(\mu-\kappa^2-pymS)_2]$  and trimeric  $[M_3(CO)_9(\mu-\kappa^2-pymS)_3]$ , although in no instance were these isolated or even detected, suggesting that tetrameric  $[M_4(CO)_{12}(\mu \kappa^3\text{-}pymS)_4]$  is the most thermodynamically stable product. Reactivity studies of **1–2** with various mono- and bidentate ligands have revealed that the metal-nitrogen bonds in these complexes are relatively weak as in every case sulfur-bound mononuclear complexes were produced. With these the pyrimidine-2-thiolate ligand showed two types of coordination mode, namely mono- or bidentate. Reactions of **1–2** with  $[Os_3(CO)_{10}(NCMe)_2]$  leads to the rational formation of 62-electron tetranuclear mixed-metal butterfly clusters with the pyrimidine-2-thiolate ligand capping a triangular face. In contrast, with  $Ru_3(CO)_{12}$  although tetrameric complexes were also prepared, these result from the cleavage of the carbon-sulfur bond affording sulfido-bridged tetranuclear mixed metal complexes.

# Experimental

### Methods and materials

Metal carbonyls (Strem) and pyrimidine-2-thiol (Aldrich) were used as received. All reactions were carried out under a nitrogen atmosphere unless otherwise stated. Reagent grade solvents were freshly distilled from appropriate drying agents prior to use. Infrared spectra were recorded on a Shimadzu FTIR 8101 spectrophotometer. NMR spectra were recorded on a Bruker DPX 400 instrument. Mass spectra were recorded on a Varian Mat 312 mass spectrometer. Elemental analyses were performed by the microanalytical laboratories, University College London. The cluster  $[Os_3(CO)_{10}(NCMe)_2]^{46}$  was prepared according to a published procedure.

### Syntheses

**Reaction of Re<sub>2</sub>(CO)<sub>10</sub> with pymSH.** A CH<sub>2</sub>Cl<sub>2</sub> solution (50 mL) of Re<sub>2</sub>(CO)<sub>10</sub> (400 mg, 0.613 mmol), Me<sub>3</sub>NO (92 mg, 1.23 mmol) and pyrimidine-2-thiol (137 mg, 1.22 mmol) was stirred at room temperature for 48 h during which time the colour of the reaction mixture changed from pale yellow to orange. The solution was then filtered through a short silica column (4 cm) to remove excess Me<sub>3</sub>NO. The solvent was removed under reduced pressure and the residue recrystallised from acetone–ethanol at 4 °C to give [Re<sub>4</sub>(CO)<sub>12</sub>( $\mu$ -κ<sup>3</sup>-pymS)<sub>4</sub>] (1) (318 mg, 68%) as orange crystals. Anal. calcd for C<sub>28</sub>H<sub>12</sub>N<sub>8</sub>O<sub>12</sub>Re<sub>4</sub>S<sub>4</sub>: C 22.04, H 0.79, N 7.35. Found (%): C 22.36, H 0.87, N 7.43. IR ( $v_{CO}$  CH<sub>2</sub>Cl<sub>2</sub>): 2028 (vs), 1923 (s, br) cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.44 (t, *J* = 5.6 Hz, 4H), 8.82 (dd, *J* = 2.0, 5.6 Hz, 4H), 8.97 (dd, *J* = 2.0, 5.6 Hz, 4H). FAB MS: m/z 1526 (M<sup>+</sup>).

**Reaction of Mn<sub>2</sub>(CO)**<sub>10</sub> with pymSH. A solution of Mn<sub>2</sub>(CO)<sub>10</sub> (400 mg, 1.03 mmol), Me<sub>3</sub>NO (154 mg, 2.05 mmol) and pyrimidine-2-thiol (230 mg, 2.05 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (50 mL) was stirred at room temperature for 48 h during which time the colour of the reaction mixture changed from pale yellow to yellow. The solution was then filtered through a short silica column (4 cm) to remove excess Me<sub>3</sub>NO. The solvent was removed under reduced pressure and recrystallisation of the residue from acetone–hexane at 4 °C afforded [Mn<sub>4</sub>(CO)<sub>12</sub>( $\mu$ - $\kappa$ <sup>3</sup>-pymS)<sub>4</sub>] (2) (366 mg, 72%) as yellow crystals. Anal. calcd for C<sub>28</sub>H<sub>12</sub>Mn<sub>4</sub>N<sub>8</sub>O<sub>12</sub>: C 33.61, H 1.21, N 11.20. Found (%): C 33.98, H 1.33, N 11.31. IR ( $\nu_{co.}$  CH<sub>2</sub>Cl<sub>2</sub>):

2027 (vs), 1934 (s, br) cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  6.63 (s, 4H), 8.46 (s, 4H), 8.61 (s, 4H). FAB MS: m/z 1000 (M<sup>+</sup>).

**Reaction of 2 with PPh<sub>3</sub>.** To a  $CH_2Cl_2$  solution (40 mL) of **2** (100 mg, 0.100 mmol) was added PPh<sub>3</sub> (105 mg, 0.401 mmol) and the mixture was then stirred for 72 h at room temperature. The solvent was removed by rotary evaporation and the residue chromatographed by TLC on silica gel. Elution with hexane- $CH_2Cl_2$  (3 : 7, v/v) developed two bands. The major band gave [Mn(CO)<sub>3</sub>(PPh<sub>3</sub>)( $\kappa^2$ -pymS)] (3) (113 mg, 55%) as yellow crystals after recrystallisation from hexane- $CH_2Cl_2$  at 4 °C while the content of the minor band was too small for characterization. Anal. calcd for  $C_{25}H_{18}MnN_2O_3PS$ : C 58.60, H 3.54, N 5.47. Found (%): C 58.92, H 3.57, N 5.52. IR ( $v_{CO}$  CH<sub>2</sub>Cl<sub>2</sub>): 2026 (vs), 1944 (s, br), 1913 (s, br) cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.93 (s, 1H), 7.82–7.40 (m, 16H), 6.37 (s, 1H). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  58.3 (s). FAB MS: m/z 512 (M<sup>+</sup>).

**Reaction of 1 with bipy.** A CH<sub>2</sub>Cl<sub>2</sub> solution (40 mL) of 1 (100 mg, 0.066 mmol) and 2,2'-bipyridine (42 mg, 0.269 mmol) was heated to reflux for 24 h. The solvent was removed under reduced pressure and the residue chromatographed by TLC on silica gel. Elution with hexane–acetone (4 : 1, v/v) developed two bands. The first band gave [Re(CO)<sub>3</sub>( $\kappa^2$ -bipy)( $\kappa^1$ -pymS)] (4) (87 mg, 62%) as red crystals after recrystallisation from hexane–acetone at 4 °C while the content of the second band was too small for characterization. Anal. calcd for C<sub>17</sub>H<sub>11</sub>N<sub>4</sub>O<sub>3</sub>ReS: C 37.98, H 2.06, N 10.42. Found (%): C 38.29, H 2.15, N 10.53. IR ( $\nu_{CO}$ , CH<sub>2</sub>Cl<sub>2</sub>): 2018 (vs), 1919 (s, br), 1898 (s, br) cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  6.61 (t, J = 4.8 Hz, 1H), 7.45 (t, J = 5.6 Hz, 2H), 8.00 (t, J = 5.6 Hz, 2H), 8.15 (d, J = 5.6 Hz, 2H), 8.20 (d, J = 5.6 Hz, 2H), 9.18 (d, J = 4.8 Hz, 2H). FAB MS: m/z 538 (M<sup>+</sup>).

**Reaction of 1 with phen.** A CH<sub>2</sub>Cl<sub>2</sub> solution (40 mL) of **1** (100 mg, 0.066 mmol) and 1,10-phenanthroline (48 mg, 0.267 mmol) was heated to reflux for 24 h. The solvent was removed under vacuum and the residue chromatographed by TLC on silica gel. Elution with hexane gave one major and several minor bands. The major band gave [Re(CO)<sub>3</sub>( $\kappa^2$ -phen)( $\kappa^1$ -pymS)] (5) (97 mg, 66%) as red crystals after recrystallisation from hexane–CH<sub>2</sub>Cl<sub>2</sub> at 4 °C while the contents of the minor bands were too small for characterization. Anal. calcd for C<sub>19</sub>H<sub>11</sub>N<sub>4</sub>O<sub>3</sub>ReS: C 40.64, H 1.97, N 9.98. Found (%): C 40.98, H 2.09, N 10.06. IR ( $v_{co}$ , CH<sub>2</sub>Cl<sub>2</sub>): 2017 (vs), 1919 (s, br), 1898 (s, br) cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.07 (t, J = 5.2 Hz, 1H), 7.87 (m, 2H), 8.02 (s, 2H), 8.56 (m, 4H), 9.40 (d, J = 5.02 Hz, 2H). FAB MS: m/z 562 (M<sup>+</sup>).

**Reaction of 2 with phen.** 1,10-Phenanthroline (116 mg, 0.644 mmol) was added to a  $CH_2Cl_2$  solution (40 mL) of **2** (161 mg, 0.161 mmol) and the mixture heated to reflux for 48 h. The solvent was removed under vacuum and the residue chromatographed by TLC on silica gel. Elution with hexane–acetone (3 : 2, v/v) developed one band, which gave [Mn(CO)<sub>3</sub>( $\kappa^2$ -phen)( $\kappa^1$ -pymS)] (6) (172 mg, 62%) as red crystals after recrystallisation from hexane–CH<sub>2</sub>Cl<sub>2</sub> at 4 °C. Anal. calcd for C<sub>19</sub>H<sub>11</sub>MnN<sub>4</sub>O<sub>3</sub>S: C 53.03, H 2.58, N 13.02. Found (%): C 53.41, H 2.67, N 13.11%. IR ( $v_{co}$ , CH<sub>2</sub>Cl<sub>2</sub>): 2020 (vs), 1933 (s, br), 1918 (s, br) cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  9.53 (m, 2H), 8.38 (m, 2H), 8.16 (m, 2H), 7.91 (m, 2H), 7.75 (m, 2H), 6.59 (m, 1H). FAB MS: m/z 430 (M<sup>+</sup>).

**Reaction of 2 with en.** To a  $CH_2Cl_2$  solution (40 mL) of **2** (161 mg, 0.161 mmol) was added a large excess of ethylenediamine (10 equiv.) and the mixture heated to reflux for 48 h. The solvent was removed under vacuum and the residue chromatographed by TLC on silica gel. Elution with hexane–acetone (3 : 2, v/v) developed one band, which gave [Mn(CO)<sub>3</sub>( $\kappa^2$ -en)( $\kappa^1$ -pymS)] (7) (136 mg, 68%) as yellow crystals after recrystallisation from hexane–CH<sub>2</sub>Cl<sub>2</sub> at 4 °C. Anal. calcd for C<sub>9</sub>H<sub>11</sub>MnN<sub>4</sub>O<sub>3</sub>S: C 34.85, H 3.57, N 18.06. Found (%): C 35.12, H 3.69, N 18.17%. IR ( $v_{co}$ , CH<sub>2</sub>Cl<sub>2</sub>): 2021 (vs), 1923 (s, br), 1902 (s, br) cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  8.25 (m, 2H), 6.84 (m, 1H), 4.92 (m, 4H), 2.95 (m, 4H). FAB MS: m/z 310 (M<sup>+</sup>).

**Reaction of 1 with dppm.** A toluene solution (40 mL) of 1 (100 mg, 0.066 mmol) and dppm (100 mg, 0.260 mmol) was heated to reflux for 7 h. The solvent was removed under vacuum and the residue chromatographed by TLC on silica gel. Elution with hexane–acetone (4:1, v/v) developed one major and several minor bands. The major band gave [Re(CO)<sub>3</sub>( $\kappa^1$ -pymS)( $\kappa^2$ -dppm)] (8) (85 mg, 42%) as pale yellow crystals after recrystallisation from hexane–CH<sub>2</sub>Cl<sub>2</sub> at 4 °C while the content of the minor bands were too small for characterization. Anal. calcd for C<sub>32</sub>H<sub>25</sub>N<sub>2</sub>O<sub>3</sub>P<sub>2</sub>ReS: C 50.19, H 3.29, N 3.66. Found (%): C 50.52, H 3.42, N 3.42. IR ( $\nu_{CO}$  CH<sub>2</sub>Cl<sub>2</sub>): 2027 (vs), 1934 (s, br), 1902 (s, br) cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  8.05 (m, 1H), 7.22 (m, 1H), 7.11–7.31 (m, 20H), 6.23 (m, 1H), 3.76 (m, 1H), 3.28 (m, 1H). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  13.7 (d, J = 88.4 Hz), 23.4 (d, J = 88.4 Hz). FAB MS: m/z 766 (M<sup>+</sup>).

**Reaction of 2 with dppm.** A cyclohexane solution (40 mL) of **2** (230 mg, 0.230 mmol) and dppm (340 mg, 0.885 mmol) was heated to reflux for 48 h. The solvent was removed under reduced pressure and the residue chromatographed by TLC on silica gel. Elution with hexane–acetone (6:4, v/v) developed one band which gave [Mn(CO)<sub>2</sub>( $\kappa^2$ -pymS)( $\kappa^1$ -dppm)<sub>2</sub>] (9) (241 mg, 26%) as orange crystals after recrystallisation from hexane–acetone at 4 °C. Anal. calcd for C<sub>56</sub>H<sub>47</sub>MnN<sub>2</sub>O<sub>2</sub>P<sub>4</sub>S: C 61.94, H 4.39, N 4.51. Found (%): C 62.19, H 4.47, N 4.55. IR ( $v_{CO}$ , CH<sub>2</sub>Cl<sub>2</sub>): 1923 (vs), 1848 (vs) cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  3.42 (m, 2H), 3.64 (m, 2H), 6.52 (m, 1H), 7.00–7.39 (m, 41), 7.55 (m, 1H). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  64.8 (br. s), 23.8 (sextet, J = 31.4, 56.7 Hz). FAB MS: m/z 990 (M<sup>+</sup>).

**Reaction of 1 with dppe.** A toluene solution (40 mL) of **1** (100 mg, 0.066 mmol) and dppe (105 mg, 0.264 mmol) was heated to reflux for 24 h. The solvent was removed by rotary evaporation and the residue chromatographed by TLC on silica gel. Elution with hexane–acetone (7 : 3, v/v) developed two bands. The faster moving band gave [Re(CO)<sub>2</sub>( $\kappa^2$ -pymS)( $\kappa^1$ -dppe)<sub>2</sub>] (**10**) (90 mg, 30%) as yellow crystals after recrystallisation from hexane–CH<sub>2</sub>Cl<sub>2</sub> at 4 °C while the content of the second band was too small for characterization. Anal. calcd for C<sub>58</sub>H<sub>51</sub>N<sub>2</sub>O<sub>2</sub>P<sub>4</sub>ReS: C 60.56, H 4.47, N 2.44. Found (%): C 60.92, H 4.60, N 2.47. IR ( $\nu_{CO}$ , CH<sub>2</sub>Cl<sub>2</sub>): 1919 (vs), 1844 (vs), cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  2.10 (m, 2H), 2.30 (m, 2H), 2.50 (m, 2H), 3.05 (m, 2H), 5.40 (t, *J* = 5.0 Hz, 1H), 6.25 (d, *J* = 5.0 Hz, 2H), 7.10–7.60 (m, 40H). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  35.0 (s), 47.6 (s). FAB MS: *m/z* 1150 (M<sup>+</sup>).

**Reaction of 2 with dppe.** A toluene solution (40 mL) of **2** (200 mg, 0.200 mmol) and dppe (325 mg, 0.817 mmol) was heated to reflux for 24 h. The solvent was removed by rotary evaporation and the residue chromatographed by TLC on silica gel. Elution

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 Table 1
 Crystallographic data and structure refinement for 1–7, 10, and 12

Compound	1	2	3	4	5	9	7	10	12
Empirical formula FW T/V	C <sub>30</sub> H <sub>18</sub> N <sub>8</sub> O <sub>13</sub> - Re <sub>4</sub> S <sub>4</sub> ·C <sub>2</sub> H <sub>5</sub> OH 1571.56	$C_{28}H_{12}Mn_4N_8-O_{12}S_4\cdot C_6H_{14}$ 1086.63	C <sub>25</sub> H <sub>18</sub> MnN <sub>2</sub> O <sub>3</sub> PS 512.38	C <sub>17</sub> H <sub>11</sub> N₄O <sub>3</sub> - ReS 537.56	C <sub>19</sub> H <sub>11</sub> N <sub>4</sub> O <sub>3</sub> - ReS 561.58	C <sub>19</sub> H <sub>11</sub> MnN₄O <sub>3</sub> S 430.32	C <sub>9</sub> H <sub>11</sub> MnN <sub>4</sub> O <sub>3</sub> S 310.22	4(C <sub>s8</sub> H <sub>51</sub> N <sub>2</sub> - O <sub>2</sub> P <sub>4</sub> ReS)·CH <sub>2</sub> Cl <sub>2</sub> 4685.52	C <sub>17</sub> H <sub>3</sub> N <sub>2</sub> O <sub>13</sub> - Os <sub>3</sub> ReS·H <sub>2</sub> O 1250.09
1./Ν λ/Å Crystal system	0.71073 0.71073 Monoclinic	0.71073 0.71073 Triclinic	0.71073 0.71073 Monoclinic	290(2) 0.71073 Monoclinic	290(2) 0.71073 Monoclinic	1.50(2) 0.71073 Monoclinic	0.71073 0.71073 Monoclinic	0.71073 0.71073 Orthorhombic	0.71073 0.71073 Monoclinic
Space group a/Å	$P2_1/c$ 21.186(3)	$P\bar{1}$ 10.7879(3)	$P2_1/c$ 9.8649(5)	$P2_1/c$ 6.928(2)	$P2_1/n$ 7.3136(2)	$P2_1/c$ 14.0795(3)	$P2_1/c$ 8.9273(2)	<i>Pnma</i> 22.3720(4)	P2 <sub>1</sub> /n 12.2398(7)
$b/\AA$ $c/\AA$	15.700(6) 13.832(6)	14.2265(4) 14.6379(4)	10.3489(5) 22.836(1)	16.657(4) 15.107(2)	13.3150(4) 18.5088(6)	10.4855(3) 12.2960(2)	12.1119(2) 12.5169(2)	22.5986(5) 10.7794(2)	13.3305(6) 16.5412(9)
$\alpha ^{\prime \circ}$	90 100.76(2) 90	85.054(2) 80.807(2) 75.568(2)	90 95.086(1) 90	90 94.71(3) 90	90 96.455(2) 90	90 91.237(2) 90	90 98.614(1) 90	06 06 00	90 103.210(3) 90
$V/\hat{A}^3$	4520(3) 4	2142.9(1)	2322.1(2) 4	1737.4(7) 4	1790.97(9) 4	1814.84(7) 4	1338.14(4) 4	5449.8(2) 1	2627.5(2) 4
$D_{ m calcl}/ m mg\ m^{-3}$ $\mu\ ( m MoKlpha)/ m mm^{-1}$ F(000)	2.309 10.926 2888	2 1.684 1.415 1092	1.466 0.757 1048	2.055 7.139 1024	2.083 6.931 1072	1.575 0.871 872	1.540 1.147 632	1.428 2.453 2362	3.160 19.201 2208
Crystal size/mm A range/°	$0.30 \times 0.25 \times 0.20$ 1 96-76 41	$0.25 \times 0.22 \times 0.20$ 2.11-27.51	$0.50 \times 0.15 \times 0.05$ 1 79-28 28	$0.10 \times 0.08 \times 0.07$ 2.45-25.28	$0.20 \times 0.15 \times 0.07$ 3 06-27 47	$0.25 \times 0.22 \times 0.20$ 1 45-77 49	$0.20 \times 0.20 \times 0.18$ 231-2750	$0.20 \times 0.10 \times 0.10$ 1 87-77 47	$0.25 \times 0.15 \times 0.10$ 1 88-75 17
Limiting indices	$-26 \le h \ge 0$ , $-19 \le k \ge 19$ ,	$-13 \le h \ge 13$ , $-18 \le k \ge 18$ ,	$-12 \le h \ge 12$ , $-13 \le k \ge 13$ ,	$-8 \le h \ge 8,$ $0 \le k \ge 20,$	$-9 \le h \ge 9$ , $-17 \le k \ge 17$ ,	$-17 \le h \ge 18$ , $-13 \le k \ge 13$ ,	$-11 \le h \ge 10$ , $-15 \le k \ge 15$ ,	$-29 \le h \ge 29,$ $-29 \le k \ge 29,$	$-14 \le h \ge 14$ , $0 \le k \ge 15$ ,
Reflections	$-16 \le l \ge 17$ 18 556	$-18 \le k \ge 18$ 54 592	$-30 \le l \ge 30$ 20 176	$0 \le l \ge 18$ $3136$	-23 ≤ l ≥ 24 11 414	$-15 \le k \ge 15$ 13 680	$-16 \le l \ge 16$ 35 600	- 9 ≤ 1 ≥ 9 51 674	$0 \le l \ge 19$ $4703$
Independent	9234 (0.0739)	9745 (0.0749)	5542 (0.0289)	3136 (0.0000)	4073 (0.0718)	4147 (0.0439)	3077 (0.0639)	5279 (0.0526)	4703 (0.0000)
Max. and min. transmission Data/restraints/	0.2186 and 0.1381 9234/0/537	0.7650 and 0.7186 9745/0/553	0.9631 and 0.7032 5542/0/298	0.6349 and 0.5354 3136/0/235	0.6426 and 0.3378 4073/0/253	0.8450 and 0.8116 4147/0/253	0.8201 and 0.8030 3077/0/163	0.7915 and 0.6397 5279/6/334	0.2497 and 0.0864 4703/0/343
parameters Goodness of fit	1.016	1.039	1.063	1.072	1.017	1.020	1.016	1.095	0.976
Final R indices [ $I > 2\sigma(I)$ ] R indices (all data) Largest difference	$R_1 = 0.0387$ , w $R_2 = 0.0924$ $R_1 = 0.1056$ , w $R_2 = 0.1105$ 2.174 and -1.221	$R_1 = 0.0434,$ w $R_2 = 0.1076$ $R_1 = 0.0721,$ w $R_2 = 0.1201$ 0.806 and -0.569	$R_1 = 0.0360,$ w $R_2 = 0.0884$ $R_1 = 0.0403,$ w $R_2 = 0.0909$ 0.565 and -0.247	$R_1 = 0.0262,$ w $R_2 = 0.0721$ $R_1 = 0.0306,$ w $R_2 = 0.0737$ 0.809 and -0.846	$R_1 = 0.0443,$ w $R_2 = 0.0885$ $R_1 = 0.0795,$ w $R_2 = 0.1082$ 1.919 and -1.967	$R_1 = 0.0395$ , w $R_2 = 0.0915$ $R_1 = 0.0672$ , w $R_2 = 0.1024$ 0.271 and -0.368	$R_1 = 0.0343$ , w $R_2 = 0.0821$ $R_1 = 0.0557$ , w $R_2 = 0.0907$ 0.257 and -0.386	$R_1 = 0.0352,$ w $R_2 = 0.0746$ $R_1 = 0.0440,$ w $R_2 = 0.0783$ 0.644 and -1.999	$R_1 = 0.0377,$ wR <sub>2</sub> = 0.0859 R <sub>1</sub> = 0.0865, wR <sub>2</sub> = 0.0940 1.647 and -1.650
In peak anu hole∕e Å-³									

with hexane–acetone (3 : 2, v/v) developed one band which gave  $[Mn(CO)_2(\kappa^2-pymS)(\kappa^2-dppe)]$  (11) (189 mg, 38%) as orange crystals after recrystallisation from hexane–acetone at 4 °C. Anal. calcd for C<sub>32</sub>H<sub>27</sub>MnN<sub>2</sub>O<sub>2</sub>P<sub>2</sub>S: C 67.88, H 4.78, N 2.83. Found (%): C 68.22, H 4.90, N 2.89. IR ( $v_{CO}$ , CH<sub>2</sub>Cl<sub>2</sub>): 1937 (vs), 1858 (vs) cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  2.01–3.36 (m, 4H), 6.48 (m, 1H), 7.02– 7.88 (m, 21H), 8.19 (m, 1H). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  98.9 (s), 77.6 (s). FAB MS: m/z 620 (M<sup>+</sup>).

**Reaction of 1 with [Os\_3(CO)\_{10}(NCMe)\_2].** A benzene solution (40 mL) of  $[Os_3(CO)_{10}(NCMe)_2]$  (250 mg, 0.268 mmol) and **1** (100 mg, 0.066 mmol) was heated to reflux for 3 h. The solvent was removed by rotary evaporation and the residue chromatographed by TLC on silica gel. Elution with hexane–acetone (4 : 1, v/v) gave one major and several minor bands. The major band afforded [ReOs<sub>3</sub>(CO)<sub>13</sub>( $\mu_3$ - $\kappa^2$ -pymS)](**12**) (130 mg, 40%) as red crystals from hexane–CH<sub>2</sub>Cl<sub>2</sub> at 4 °C while the content of the second band was too small for characterization. Anal. calcd for C<sub>17</sub>H<sub>3</sub>N<sub>2</sub>O<sub>13</sub>Os<sub>3</sub>ReS: C 16.57, H 0.25, N 2.27. Found (%): C 16.74, H 0.28, N 2.33. IR ( $\nu_{CO}$ , CH<sub>2</sub>Cl<sub>2</sub>): 2112 (m), 2044 (vs), 2029 (m), 2013 (m), 1985 (w), 1965 (m, br) cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.31 (t, J = 5.6 Hz, 1H), 8.80 (dd, J = 2.4, 5.6 Hz, 1H), 9.66 (dd, J = 2.4, 5.6 Hz, 1H). FAB MS: m/z 1234 (M<sup>+</sup>).

**Reaction of 2 with [Os\_3(CO)\_{10}(NCMe)\_2].** A benzene solution (40 mL) of  $[Os_3(CO)_{10}(NCMe)_2]$  (380 mg, 0.407 mmol) and **2** (100 mg, 0.100 mmol) was heated to reflux for 3 h. The solvent was removed under reduced pressure and the residue chromatographed by TLC on silica gel. Elution with hexane–acetone (4 : 1, v/v) gave one major and several minor bands. The major band afforded  $[MnOs_3(CO)_{13}(\mu_3-\kappa^2-pymS)]$  (**13**) (136 mg, 31%) as red crystals from hexane–CH<sub>2</sub>Cl<sub>2</sub> at 4 °C while the content of the second band was too small for characterization. Anal. calcd for C<sub>17</sub>H<sub>3</sub>MnN<sub>2</sub>O<sub>13</sub>Os<sub>3</sub>S: C 18.55, H 0.27, N 2.54. Found (%): C 18.79, H 0.31, N 2.58. IR ( $v_{co}$ , CH<sub>2</sub>Cl<sub>2</sub>): 2110 (m), 2042 (vs), 2027 (m), 2002 (m), 1981 (w), 1961 (m, br) cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.20 (s, br, 1H), 8.80 (s, br, 1H), 10.20 (s, br, 1H). FAB MS: m/z 1102 (M<sup>+</sup>).

**Reaction of 1 with Ru<sub>3</sub>(CO)**<sub>12</sub>. A toluene solution (40 mL) of Ru<sub>3</sub>(CO)<sub>12</sub> (256 mg, 0.400 mmol) and **1** (154 mg, 0.101 mmol) was heated to reflux for 1 h. The solvent was removed *in vacuo* and the residue chromatographed by TLC on silica gel. Elution with hexane–acetone (4 : 1, v/v) developed three bands. The first band was unreacted Ru<sub>3</sub>(CO)<sub>12</sub> (trace). The second band afforded [ReRu<sub>3</sub>(CO)<sub>14</sub>( $\mu_4$ -S)( $\mu_2$ - $\kappa^1$ : $\eta^1$ -pym)] (**14**) (176 mg, 44%) as red crystals from hexane–CH<sub>2</sub>Cl<sub>2</sub> at 4 °C while the content of the third band was too small for characterization. Anal. calcd for C<sub>18</sub>H<sub>3</sub>N<sub>2</sub>O<sub>14</sub>ReRu<sub>3</sub>S: C 21.78, H 0.30, N 2.82. Found (%): C 21.93, H 0.31, N 2.84. IR ( $\nu_{CO}$ , CH<sub>2</sub>Cl<sub>2</sub>): 2114 (w), 2080 (m), 2056 (vs), 2044 (s), 2003 (m), 1975 (m), 1955 (m) cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>) for major isomer:  $\delta$  7.69 (s, 1H), 7.51 (s, 1H), 7.11 (s, 1H). FAB MS: m/z 993 (M<sup>+</sup>).

**Reaction of 2 with Ru<sub>3</sub>(CO)**<sub>12</sub>. A toluene solution (40 mL) of Ru<sub>3</sub>(CO)<sub>12</sub> (256 mg, 0.400 mmol) and **2** (100 mg, 0.100 mmol) was heated to reflux for 30 min. The solvent was removed by rotary evaporation and the residue chromatographed by TLC on silica gel. Elution with hexane–acetone (4 : 1, v/v) developed three bands. The first band was unreacted Ru<sub>3</sub>(CO)<sub>12</sub> (trace). The second band afforded [MnRu<sub>3</sub>(CO)<sub>14</sub>( $\mu_4$ -S)( $\mu$ - $\kappa$ <sup>1</sup>: $\eta$ <sup>1</sup>-pym)] (**15**) (159 mg, 46%) as red crystals from hexane–CH<sub>2</sub>Cl<sub>2</sub> at 4 °C while the content

of the third band was too small for characterization. Anal. calcd for  $C_{18}H_3MnN_2O_{14}Ru_3S$ : C 25.10, H 0.35, N 3.25. Found (%): C 25.37, H 0.38, N 3.29. IR ( $\nu_{CO}$  CH<sub>2</sub>Cl<sub>2</sub>): 2118 (w), 2081 (m), 2058 (vs), 2046 (s), 2006 (m), 1979 (m), 1961 (m), 1940 (m) cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>) for major isomer:  $\delta$  6.95 (s, 1H), 7.86 (s, 1H), 9.51 (s, 1H). FAB MS: m/z 863 (M<sup>+</sup>).

### Crystallography

Single crystals were mounted on fibres and diffraction data collected at low temperature (see Table 1) on Enraf Nonius CAD4 (1, 2, 4, 10), Nonius Kappa CCD (5, 6, 7, 12) and Bruker AXS SMART APEX CCD (3) diffractometers using MoK $\alpha$  radiation ( $\lambda = 0.71073$  Å). Data collection, indexing and initial cell refinements were all done using SMART<sup>47</sup> software. Data reduction was accomplished with SAINT<sup>48</sup> software and the DIFABS<sup>49</sup> and SADABS<sup>50</sup> program was used to apply empirical absorption corrections. The structures were solved by direct methods<sup>51</sup> and refined by full matrix least-squares.<sup>52</sup> All nonhydrogen atoms were refined anisotropically and hydrogen atoms were taken from International Tables for X-ray Crystallography.<sup>53</sup> Additional details of data collection and structure refinement are given in Table 1.

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