# Tetranuclear [Rh4(µ-PyS<sub>2</sub>)<sub>2</sub>(diolefin)<sub>4</sub>] Complexes as Building Blocks for New Inorganic Architectures: Synthesis of Coordination Polymers and Heteropolynuclear Complexes with Electrophilic d<sup>8</sup> and d<sup>10</sup> Metal Fragments

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#### Abstract

The reaction of  $[Rh_4(\mu-PyS_2)_2(cod)_4]$  (PyS<sub>2</sub> = 2,6-pyridine dithiolate, cod = 1,5-cyclooctadiene) with cationic complex [Rh<sub>4</sub>(µ-PyS<sub>2</sub>Me)<sub>2</sub>(cod)<sub>4</sub>][CF<sub>3</sub>SO<sub>3</sub>]<sub>2</sub> with two CF<sub>3</sub>SO<sub>3</sub>Me gave the 6thiomethylpyridine-2-thiolate bridging ligands from the attack of Me<sup>+</sup> at the terminal sulfur atoms of the starting material. Under identical conditions  $[Rh_4(\mu-PyS_2)_2(tfbb)_4]$ (tfbb =tetrafluorobenzobarrelene) reacted with CF<sub>3</sub>SO<sub>3</sub>Me to give the mixed-ligand complex  $[Rh_4(\mu-PyS_2)(\mu-PyS_2)]$  $PyS_2Me$ )(tfbb)<sub>4</sub>][CF<sub>3</sub>SO<sub>3</sub>]. The nucleophilicity of the bridging ligands in the complexes [Rh<sub>4</sub>( $\mu$ heteropolynuclear  $PyS_2$ (diolefin)<sub>4</sub>] was exploited to prepare species. Reactions with  $[Au(PPh_3)(Me_2CO)][ClO_4]$ the hexanuclear complexes  $[(PPh_3)_2Au_2Rh_4(\mu$ gave  $PyS_2)_2(diolefin)_4][ClO_4]_2$  (diolefin = cod, tfbb (4)). The structure of 4, solved by X-ray diffraction methods, showed the coordination of the [Au(PPh<sub>3</sub>)]<sup>+</sup> fragments to the peripheral sulfur atoms in  $[Rh_4(\mu-PyS_2)_2(diolefin)_4]$  along with their interaction with the neighbor rhodium atoms. Neutral coordination polymers of formula  $[ClMRh_4(\mu-PyS_2)_2(diolefin)_4]_n$  (M = Cu, Au) result from the selfassembly of alternating  $[Rh_4(\mu-PyS_2)_2(diolefin)_4]$  ( $[Rh_4]$ ) blocks and MCl linkers. The formation of the infinite polymetallic chains was found to be chiroselective for M = Cu; one particular chain contains exclusively homochiral [Rh4] complexes. Cationic heterometallic coordination polymers of formula  $[MRh_4(\mu-PyS_2)_2(diolefin)_4]_n [BF_4]_n (M = Cu, Ag) and [Rh_5(\mu-PyS_2)_2(diolefin)_5]_n [BF_4]_n result from the$ reactions of [Rh<sub>4</sub>] with [Cu(CH<sub>3</sub>CN)<sub>4</sub>]BF<sub>4</sub>, AgBF<sub>4</sub>, and [Rh(diolefin)(Me<sub>2</sub>CO)<sub>2</sub>]BF<sub>4</sub>, respectively. The heterometallic coordination polymers exhibit a weak electric conductivity in the solid state in the range 1.2-2.8 x 10<sup>-7</sup> S cm<sup>-1</sup>.

#### Introduction

The molecular self-assembly of coordination polymers and supramolecular assemblies through metalligand coordination is a powerful method in the design of new materials with promising physicochemical properties of potential application in technology.<sup>1</sup> The development of coordination polymer chemistry has given rise to many remarkable inorganic architectures through the self-assembly of suitable polydentate ligands with metal ions or unsaturated metal complexes.<sup>2</sup> The design of the ligand is crucial for this purpose, since the dimensionality and topology of the final assemblies are predominantly controlled by the coordination preferences of the metal center and the location of the donor sites in the organic ligand.<sup>3</sup>

An alternative approach to the synthesis of coordination polymers and supramolecules is the use of transition metal complexes as building blocks. Metal-containing ligands with uncoordinated donor atoms can be induced to self-assemble with other metal ions or unsaturated metal complexes through the free coordination donors.<sup>4</sup> In this context, mixed-metal coordination polymers have been assembled using the rod-shaped dicyanoargentate(I) complex and tetracyanoaurate(III) as building blocks.<sup>5</sup> Mononuclear cyanoisocyanoarene and pyridylphenylisocyanide metal complexes, bearing respectively cyano and pyridyl groups in peripheral sites, are also effective building blocks for coordination polymers.<sup>6</sup> Similarly, one-dimensional Cu(II)-Ag(I) mixed-metal chains with 2-methylpyrazine-5-carboxylate spacers, have been obtained from a mononuclear Cu(II) complex having free donor sites and silver(I) salts.<sup>7</sup> Dinuclear species as connection devices for self-assembly have scarcely been exploited. Very recently, reports from several groups describe the use of the Rh<sub>2</sub><sup>4+</sup> core as a building block to form both cyclic supramolecules and coordination polymers by condensation with appropriate bidentate ligands.<sup>8</sup>

As a result of our interest in the design of effective polydentate ligands for the construction of polynuclear complexes<sup>9</sup> we have prepared the tetranuclear  $[M_4(\mu-PyS_2)_2(diolefin)_4]$  (M= Rh, Ir) complexes ([M<sub>4</sub>]) supported by two tridentate 2,6-pyridinedithiolate (PyS<sub>2</sub><sup>2-</sup>) bridging ligands acting as six electron donors.<sup>10</sup> The rhodium and iridium tetranuclear complexes [M<sub>4</sub>] are redox-active

precursors of mixed-valence paramagnetic  $[M_4]^+$  complexes.<sup>11</sup> They also behave as encapsulating agents for the thallium(I) ion to give the cationic pentametallic species  $[TIM_4(\mu-PyS_2)_2(diolefin)_4]^+$ through a great change of the coordination mode of the bridging 2,6-dimercaptopyridine ligands and the formation of two Tl-M bonds.<sup>12</sup> A preliminary test on the capability of the tetranuclear  $[Rh_4(\mu PyS_2)_2(cod)_4]$  complex to act as a metalloligand, due to the presence of two available coordination donor sites at the peripheral sulfur atoms, has lead to the synthesis of the polymer  $[ClCuRh_4(\mu PyS_2)_2(cod)_4]_n$  (cod =1,5-cyclooctadiene) fully characterized by a crystal structure determination.<sup>13</sup> Thus, the tetranuclear complexes can be envisaged as building blocks for new inorganic assemblies by adding suitable metal centers and assuming that the structure of the tetranuclear framework is maintained. Herein we describe the construction of discrete heteropolynuclear complexes and onedimensional coordination polymers obtained by reaction of the rhodium complexes  $[Rh_4(\mu PyS_2)_2(diolefin)_4]$  with electrophilic d<sup>8</sup> and d<sup>10</sup> metal complexes.

#### **Results and discussion**

Reactions of  $[Rh_4(\mu-PyS_2)_2(diolefin)_4]$  ( $[M_4]$ ) with  $CF_3SO_3Me$ . Synthesis of 6-thiomethylpyridine-2-thiolate cationic complexes.

Looking for the nucleophilic centers in the complexes [M<sub>4</sub>], we reacted them with the electrophilic Me<sup>+</sup> to assess about the donor atoms and their possible stereochemistry for further reactions with metal centers. From the reaction of [Rh<sub>4</sub>( $\mu$ -PyS<sub>2</sub>)<sub>2</sub>(cod)<sub>4</sub>] with CF<sub>3</sub>SO<sub>3</sub>Me the cationic tetranuclear species [Rh<sub>4</sub>( $\mu$ -PyS<sub>2</sub>Me)<sub>2</sub>(cod)<sub>4</sub>][CF<sub>3</sub>SO<sub>3</sub>]<sub>2</sub> (**1**) was isolated in good yield as a red microcrystalline solid. The attack of Me<sup>+</sup> occurred at the terminal sulfur atoms of the complex [Rh<sub>4</sub>( $\mu$ -PyS<sub>2</sub>)<sub>2</sub>(cod)<sub>4</sub>] to produce two 6-thiomethylpyridine-2-thiolate bridging ligands. Thus, complex **1** behaves as a 2:1 electrolyte in acetone, and the thiomethyl groups were observed as singlets at  $\delta$  2.80 ppm in the <sup>1</sup>H and at 17.9 ppm in the <sup>13</sup>C{<sup>1</sup>H} NMR spectra. Moreover, both bridging 6-thiomethylpyridine-2-thiolate ligands were found to be equivalent, while the olefin carbons of the four 1,5-cyclooctadiene ligands displayed eight doublets in the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum, evidencing that the cation possesses a *C*<sub>2</sub> symmetry.

Compound **1** is apparently static while the parent complex  $[Rh_4(\mu-PyS_2)_2(cod)_4]$  is fluxional; the motion, affecting to the external cod ligands, is associated to the lonely electron pairs on the outer sulfur atoms.<sup>10</sup> The formation of the thiomethyl groups fixes an electron pair per sulfur and, in consequence, complex **1** becomes rigid.

The methylation of the 2,6-pyridinedithiolate bridges in  $[Rh_4(\mu-PyS_2)_2(cod)_4]$  resulted to be a stereoselective process, since complex **1** was obtained as one single diastereoisomer. The tetranuclear compound  $[Rh_4(\mu-PyS_2)_2(cod)_4]$  exits as a pair of enantiomers, which can be designed as  $(R_S,R_S)$ - $[Rh_4]$  and  $(S_S,S_S)$ - $[Rh_4]$ , since the two bridging sulfur atoms are stereogenic. Upon methylation, the two terminal sulfur atoms also become chiral centers; up to six different stereoisomers could be produced depending on the relative disposition of the thiomethyl groups in both enantiomers. However, since the symmetry found for **1** is  $C_2$ , both sulfur atoms of the thiomethyl groups should have identical configuration, and therefore complex 1 resulted to be a single enantiomeric pair. Assuming that the thiomethyl groups were directed away from the bulky 1,5-cyclooctadiene ligands on the neighboring rhodium atoms, complex **1** would exist as the enantiomeric pair  $(R_S,R_S,S_S,S_S)$ - $(1)/(S_S,S_S,R_S,R_S)$ -(1),<sup>14</sup> the former being depicted in Chart 1 1



Chart 1. Proposed structures of complexes 1 and 2.

The mixed-ligand complex  $[Rh_4(\mu-PyS_2)(\mu-PyS_2Me)(tfbb)_4][CF_3SO_3]$  (2) was obtained as a dark red microcrystalline solid by reaction of  $[Rh_4(\mu-PyS_2)_2(tfbb)_4]$  with CF\_3SO\_3Me under identical conditions than for the cod complex. It is noticeable that in this case only one of the bridging ligands was methylated and, consequently, the complex 2 possesses 6-thiomethylpyridine-2-thiolate and 2,6-pyridinedithiolate bridges (Chart 1 2). As expected, the <sup>1</sup>H NMR spectra of 2 showed six resonances for the aromatic protons of the two different bridging ligands. The combination of the H,H-COSY spectrum, which allowed the identification of the two sets of three resonances for the pyridine rings, with the detection of a NOE effect (5%) between the protons of the thiomethyl group at  $\delta$  2.79 ppm and the signal at  $\delta$  6.86 ppm allowed the full assignment of the aromatic resonances.

Attempts to prepare the complex  $[Rh_4(\mu-PyS_2Me)_2(tfbb)_4]^{2+}$  by reacting  $[Rh_4(\mu-PyS_2)_2(tfbb)_4]$  with CF<sub>3</sub>SO<sub>3</sub>Me in excess were also unsuccessful. Compound **2** was isolated again under these conditions, but in lower yield. This result suggests a weaker nucleophilicity of the terminal sulfur atoms in  $[Rh_4(\mu-PyS_2)_2(tfbb)_4]$  than in the analogous cod complex, which could be attributed to the stronger  $\pi$ -acceptor character of the tfbb ligands. The partial methylation in **2** *versus* the full methylation in **1** is a clear evidence for the interplay between metals and ligands leading to an electronic communication between the sulfurs. On the other hand, both experiments corroborate the ability of the tetranuclear complexes to engage electron pairs on the outer sulfur atoms with electrophiles in a stereoselective way.

Reaction of  $[Rh_4(\mu-PyS_2)_2(diolefin)_4]$  with  $M(PPh_3)^+$  (M = Ag, Au). Syntheses of discrete heteropolynuclear complexes.

Two further examples confirm the potential of the tetranuclear complexes to act as bidentate ligands for appropriate metal centers. Thus, the reaction of  $[Rh_4(\mu-PyS_2)_2(cod)_4]$  with two molar equiv. of the solvated species  $[Au(PPh_3)(Me_2CO)][ClO_4]$  gave the heteropolynuclear complex  $[(PPh_3)_2Au_2Rh_4(\mu-PyS_2)_2(cod)_4][ClO_4]_2$  (3), which was isolated as a red microcrystalline solid in good yield. Similarly, the hexanuclear complex  $[(PPh_3)_2Au_2Rh_4(\mu-PyS_2)_2(tfbb)_4][ClO_4]_2$  (4) was isolated from the reaction of  $[Rh_4(\mu-PyS_2)_2(tfbb)_4]$  with  $[Au(PPh_3)(Me_2CO)][ClO_4]$  as violet microcrystals. Both complexes behave as 2:1 electrolytes in acetone, although the peaks of largest m/z observed in the FAB<sup>+</sup> mass spectra corresponded to the ions [Rh<sub>4</sub>]-Au(PPh<sub>3</sub>)<sup>+</sup> (100%). The two bridging pyridine-2,6-dithiolate ligands and the PPh<sub>3</sub> groups were found to be equivalent in the <sup>1</sup>H NMR and <sup>31</sup>P{<sup>1</sup>H} NMR spectra of the complexes **3-4**, respectively, in agreement with structures with a  $C_2$  symmetry.

The molecular structure of compound [(PPh<sub>3</sub>)<sub>2</sub>Au<sub>2</sub>Rh<sub>4</sub>( $\mu$ -PyS<sub>2</sub>)<sub>2</sub>(tfbb)<sub>4</sub>][ClO<sub>4</sub>]<sub>2</sub> (**4**) determined by Xray methods is shown in Figure 1. Selected bond distances and angles are listed in Table 1. Compound **4** is hexanuclear resulting from the coordination of two Au(PPh<sub>3</sub>)<sup>+</sup> fragments to the peripheral sulfur atoms of the tetranuclear complex [Rh<sub>4</sub>( $\mu$ -PyS<sub>2</sub>)<sub>2</sub>(tfbb)<sub>4</sub>]. Both 2,6-pyridinedithiolate ligands are bonded to the four rhodium centers and to one gold(I) atom, acting as eight-electron donors. The C-S bond distances (range 1.752-1.790(11) Å), corresponding to a bond order near to 1, suggest the major presence of the thiolate resonant hybrid of the PyS<sub>2</sub><sup>2-</sup> ligands rather than the thione upon coordination to the Au atoms. The rhodium atoms exhibit a slightly distorted square-planar geometry while the coordination environment of the gold(I) centers is roughly linear. It is noticeable that the Au(PPh<sub>3</sub>) fragments are directed away from the Rh(cod) fragments, as proposed for complex **1**. In consequence, compound **4** exists in the solid state as the enantiomeric pair ( $R_S, R_S, S_S, S_S$ )-(**4**)/( $S_S, S_S, R_S, R_S$ )-(**4**).<sup>14</sup>



Figure 1. Molecular structure of  $[(PPh_3)_2Au_2Rh_4(\mu-PyS_2)_2(tfbb)_4][ClO_4]_2(4)$ .

An interesting structural feature of **4** concerns the intermetallic separations. Although the rhodiumrhodium distances (range 3.0720-3.3509(18) Å) are shorter than those found in the complex [Rh<sub>4</sub>( $\mu$ -PyS<sub>2</sub>)<sub>2</sub>(cod)<sub>4</sub>] (3.9210(6) Å and 3.1435(5) Å), the shortening of the internal intermetallic distance is notable. However, the shortest intermetallic separation in **4**, 3.0627(10) Å, corresponds to the Au...Rh separation. This distance, although clearly longer than those found in complexes with rhodium(I)gold(I) bonds, is short enough to be indicative of a intermetallic interaction, and is probably a consequence of the metalophilic attraction between both closed-shell d<sup>8</sup>-d<sup>10</sup> metals.<sup>15</sup>

The attachment of Au(PPh<sub>3</sub>) groups to both terminal sulfur atoms in  $[Rh_4(\mu-PyS_2)_2(tfbb)_4]$  to give 4 contrasts with the single methylation of one pyridine-2,6-dithiolate ligand with CF<sub>3</sub>SO<sub>3</sub>Me to give  $[Rh_4(\mu-PyS_2)(\mu-PyS_2Me)(tfbb)_4]^+$  (2). The difference reflects a lesser need of electronic density on the sulfur atoms for coordination to a metal than for alkylation, in addition to the affinity of gold for the soft sulfur donor atoms.

The reactions of the tetranuclear complexes with  $[Ag(PPh_3)]ClO_4$  gave distinct results. Thus, while the reaction with  $[Rh_4(\mu-PyS_2)_2(cod)_4]$  rendered an insoluble solid analyzing as the coordination polymer (see below)  $[AgRh_4(\mu-PyS_2)_2(cod)_4]_n[ClO_4]_n$  in good yield and triphenylphosphine, the reaction with  $[Rh_4(\mu-PyS_2)_2(tfbb)_4]$  gave the mononuclear complex  $[Rh(tfbb)(PPh_3)_2]^+$  as the single isolated species. Monitoring the latter reaction by  ${}^{31}P{}^{1}H{}$  NMR spectroscopy at low temperature confirmed the complete transference of the PPh<sub>3</sub> ligands from the silver complex to Rh(tfbb)<sup>+</sup> fragments arising from the tetranuclear complexes, since the only phosphorus containing species observed was  $[Rh(tfbb)(PPh_3)_2]^+$  ( $\delta$  : 28.0 ppm; d, J\_{Rh-P}= 150 Hz).

Reactions of  $[Rh_4(\mu-PyS_2)_2(diolefin)_4]$  with MCl (M = Cu, Au),  $M^+$  (M = Ag, Cu) and  $[Rh(diolefin)]^+$ . Synthesis of coordination polymers.

We have shown<sup>13</sup> that [ClCuRh<sub>4</sub>( $\mu$ -PyS<sub>2</sub>)<sub>2</sub>(cod)<sub>4</sub>]<sub>n</sub> (**5**), obtained by reaction of [Rh<sub>4</sub>( $\mu$ -PyS<sub>2</sub>)<sub>2</sub>(cod)<sub>4</sub>] with CuCl, is a mixed-metal coordination polymer in the solid state resulting from the self-assembly of alternating [Rh<sub>4</sub>( $\mu$ -PyS<sub>2</sub>)<sub>2</sub>(cod)<sub>4</sub>] blocks and CuCl linking units, as shown in Figure 2. The related

compound  $[ClCuRh_4(\mu-PyS_2)_2(tfbb)_4]_n$  (6) was isolated as a purple solid by mixing equimolar amounts of  $[Rh_4(\mu-PyS_2)_2(tfbb)_4]$  and CuCl in dichloromethane. Looking for metal fragments other than CuCl to act as linkers in polymeric structures based on the tetranuclear  $[Rh_4]$  ligands we sought that nude cations of the Group 11 metals or complexes with two available coordination positions could also produce polymeric structures by a self-assembly process.



**Figure 2.** Crystal packing of the compound  $[ClCuRh_4(\mu-PyS_2)_2(cod)_4]_n$  (**5**) showing a short segment of two homochiral infinite chains (the labelling indicates the chirality of the sulfur atoms).

The compound [AuCl(tht)] behaves as a source of "AuCl" fragments due to the presence of the labile tetrahydrothiophene (tht) ligand. Thus, the reaction of  $[Rh_4(\mu-PyS_2)_2(tfbb)_4]$  with [AuCl(tht)] in dichloromethane (1:1 molar ratio) gave the mixed-metal coordination polymer [ClAuRh<sub>4</sub>( $\mu$ -PyS<sub>2</sub>)<sub>2</sub>(tfbb)<sub>4</sub>]<sub>n</sub> (7), which was isolated as a purple microcrystalline solid in good yield. However, the related cyclooctadiene compound [ClAuRh<sub>4</sub>( $\mu$ -PyS<sub>2</sub>)<sub>2</sub>(cod)<sub>4</sub>]<sub>n</sub> could not be obtained by this route, but a brown insoluble material with poorly reproducible analytical results was isolated from the reaction of [Rh<sub>4</sub>( $\mu$ -PyS<sub>2</sub>)<sub>2</sub>(cod)<sub>4</sub>] with four molar-equiv. of [AuCl(tht)].

The cationic mixed-metal coordination polymers containing silver(I)  $[AgRh_4(\mu-PyS_2)_2(cod)_4]_n[BF_4]_n$ (8) and  $[AgRh_4(\mu-PyS_2)_2(tfbb)_4]_n[BF_4]_n$  (9) were obtained by reaction of the complexes  $[Rh_4(\mu-PyS_2)_2(diolefin)_4]$  with AgBF<sub>4</sub>. In a similar fashion, the reaction of the complexes  $[Rh_4(\mu-PyS_2)_2(diolefin)_4]$  with  $[Cu(CH_3CN)_4]BF_4$  resulted in the formation of the coordination assemblies  $[CuRh_4(\mu-PyS_2)_2(cod)_4]_n[BF_4]_n$  (10) and  $[CuRh_4(\mu-PyS_2)_2(tfbb)_4]_n[BF_4]_n$  (11) in good isolated yields. The formation of the silver(I) complexes **8** and **9** competes with the oxidation of the corresponding rhodium tetranuclear complexes. In fact, complex **8** decomposes slowly in dichloromethane to give the paramagnetic compound  $[Rh_4(\mu-PyS_2)_2(cod)_4]BF_4$  and metallic silver.<sup>10</sup>

Neither  $[Rh_4(\mu-PyS_2)_2(cod)_4]$  nor  $[Rh_4(\mu-PyS_2)_2(tfbb)_4]$  were found able to add [RhCl(diolefin)]fragments from the complexes  $[Rh(\mu-Cl)(diolefin)]_2$  (diolefin = cod and tfbb), although homometallic coordination polymers were accessible by the reactions with cationic rhodium species with two easily replaceable ligands. Thus, addition of  $[Rh(diolefin)(Me_2CO)_2]^+$  to the corresponding tetranuclear complex in dichloromethane, resulted in the formation of the cationic coordination polymers  $[Rh_5(\mu-PyS_2)_2(cod)_5]_n[BF4]_n$  (12) and  $[Rh_5(\mu-PyS_2)_2(tfbb)_5]_n[BF4]_n$  (13), which were isolated as purple and violet microcrystalline solids in excellent yields. Attempts to apply this synthetic approach to coordination polymers made with  $[Rh_4]$  as ligands and d<sup>8</sup> centers as linkers were unsuccessful, since the syntheses resulted to be no selective. For example, the reaction of  $[Rh_4(\mu-PyS_2)_2(cod)_4]$  with  $[Ir(cod)(Me_2CO)_x]^+$  gave mixtures of compounds containing heterotetranuclear complexes  $[Rh_3Ir]$  and  $[Rh_2Ir_2]$  (FAB<sup>+</sup> MS evidence) as the result of the exchange between the added  $Ir(cod)^+$  fragment with  $Rh(cod)^+$  in the  $[Rh_4]$  complex.

# Chiroselective formation of $[ClCuRh_4(\mu-PyS_2)_2(cod)_4]_n$ .

As already mentioned, the crystal structure of  $[ClCuRh_4(\mu-PyS_2)_2(cod)_4]_n$  (5) consists of onedimensional chains that propagate along a screw two-fold axis; one particular chain contains exclusively homochiral [Rh<sub>4</sub>] building blocks.<sup>13</sup> Figure 2 shows short segments of two complementary homochiral infinite chains; the upper chain contains ( $R_S, R_S, R_S, R_S$ )-[Rh<sub>4</sub>] complexes and the lower ( $S_S, S_S, S_S, S_S$ )-[Rh<sub>4</sub>] complexes .

Since the parent compound  $[Rh_4(\mu-PyS_2)_2(cod)_4]$  exits as the pair of enantiomers  $(R_S,R_S)$ - $[Rh_4]$  and  $(S_S,S_S)$ - $[Rh_4]$  and the two peripheral sulfur atoms become chiral centers on coordination to the CuCl linkers, a chiral recognition occurs in the formation of each chain to be made exclusively either  $(R_S,R_S,R_S,R_S)$ - $[Rh_4]$  or  $(S_S,S_S,S_S,S_S)$ - $[Rh_4]$  complexes, respectively. In this case not only the two new

chiral sulfur centers possess identical chirality, but all the sulfur atoms have identical chirality in a particular chain.<sup>14</sup>

In contrast with most of the coordination polymers described herein the compound [ClCuRh<sub>4</sub>( $\mu$ - $PyS_2)_2(cod)_4]_n$  (5) is soluble in chlorinated solvents and in benzene. The fragmentation of the polymeric structure in solution becomes evident after the determination of a remarkably low molecular weight (1730) in chloroform while compound 5 is a non-electrolyte in this solvent. The crystallization of 5 leads to the formation of the infinite homochiral chains in a reversible way. Spectroscopic data in solution suggest the presence of two well defined molecular species in solution, since the aromatic region of the <sup>1</sup>H NMR spectrum in benzene-d<sub>6</sub> was outstandingly simple while the parent complex  $[Rh_4(\mu-PyS_2)_2(cod)_4]$  was not detected. Assuming that the molecular species in solution were Cl<sub>2</sub>Cu<sub>2</sub>-[Rh<sub>4</sub>] and ClCu-[Rh<sub>4</sub>]<sub>2</sub>, their combination would produce the polymeric chain. Supporting this idea, the ions ClCu<sub>2</sub>-[Rh<sub>4</sub>]<sup>+</sup> and ClCu-[Rh<sub>4</sub>]<sup>+</sup> were detected in the FAB<sup>+</sup> spectrum. In addition, the calculated molecular weight for an equimolar mixture of Cl<sub>2</sub>Cu<sub>2</sub>-[Rh<sub>4</sub>] and ClCu-[Rh<sub>4</sub>]<sub>2</sub> (1837) agrees well with the experimental observed value (1730). Moreover, the aromatic region of the <sup>1</sup>H NMR spectrum of **3** is compatible with the presence of both species in a 1:1 molar ratio. Thus, the resonances at  $\delta$  8.40, 6.90 and 6.40 ppm would correspond to the homotopic  $PyS_2^{2-}$  ligands of  $Cl_2Cu_2$ -[Rh<sub>4</sub>], whereas the two sets of resonances at  $\delta$  7.90, 6.80, 6.30 and 6.90, 6.55, 6.05 ppm can be assigned to two pairs of equivalent bridging ligands in ClCu-[Rh<sub>4</sub>]<sub>2</sub>, which is in accordance with the couplings observed by analysis of the H,H-COSY spectrum. From the above data, the species Cl<sub>2</sub>Cu<sub>2</sub>-[Rh<sub>4</sub>], with a C<sub>2</sub> axis, exists as a pair of enantiomers giving identical NMR spectra. The apparently single species detected for ClCu-[Rh<sub>4</sub>]<sub>2</sub> could be either the enantiomeric pair ClCu-(R<sub>S</sub>,R<sub>S</sub>,R<sub>S</sub>)-[Rh<sub>4</sub>]<sub>2</sub>/ClCu-(S<sub>S</sub>,S<sub>S</sub>,S<sub>S</sub>)-[Rh<sub>4</sub>]<sub>2</sub> or ClCu- $(R_S, R_S, R_S)$ -[Rh<sub>4</sub>] $(S_S, S_S, S_S)$ -[Rh<sub>4</sub>], with  $C_2$  and  $C_8$  symmetries, respectively, (Figure 3) or both assuming that the resonances were averaged by a dissociative equilibrium. Inspection of molecular models of ClCu-[Rh<sub>4</sub>]<sub>2</sub> suggests that the steric interaction between the bulky 1,5-cyclooctadiene ligands and the bridging ligands is notably reduced if they consist of homochiral tetranuclear complexes, i.e. the enantiomeric pair. As a consequence, the formation of the polymer would encompass the molecular recognition between the following chiral molecular components  $ClCu-(R_S,R_S,R_S)-[Rh_4]_2/Cl_2Cu_2-(R_S,R_S,R_S)-[Rh_4]$  and  $ClCu-(S_S,S_S,S_S)-[Rh_4]_2/Cl_2Cu_2-(S_S,S_S,S_S)-[Rh_4]$ .



**Figure 3.** Diastereoisomers of the molecular species ClCu-[Rh<sub>4</sub>]<sub>2</sub>: (a) ClCu-( $R_S, R_S, R_S$ )-[Rh<sub>4</sub>]<sub>2</sub>/ClCu-( $S_S, S_S, S_S$ )-[Rh<sub>4</sub>]<sub>2</sub> and (b) ClCu-( $R_S, R_S, R_S$ )-[Rh<sub>4</sub>]( $S_S, S_S, S_S$ )-[Rh<sub>4</sub>].

The chiroselectivity observed in the formation of the polymeric chains in **3** is an unusual example of chiral selection during the self-assembly process. Chiroselective self-assembly of [2x2] grid-type inorganic arrays with different octahedral metal centers have been reported.<sup>16</sup> Diastereoselectivity has been also observed in the self-assembly of molecular squares based on palladium and platinum square-planar complexes<sup>17</sup> and in homochiral macrocyclic dinuclear anions containing octahedral molybdenum complexes.<sup>18</sup> A related 2-D phenomenon in a supramolecular three-dimensional hydrogen-bonded network derived from diacetylene dicarboxylic acid dihydrate has been noticed.<sup>19</sup> Multiple hydrogen bonding also produces homochiral columnar structures made with alternate stacked cations [Co(en)<sub>3</sub>]<sup>3+</sup> and P<sub>3</sub>O<sub>9</sub><sup>3-</sup> anions with the  $\Lambda$  or  $\Delta$  enantiomer.<sup>20</sup>

## Characterization and properties of the coordination polymers.

The coordination polymers have been characterized by elemental microanalyses and FAB<sup>+</sup> MS. A diagnostic for the coordination polymers are the respective FAB<sup>+</sup> MS, since characteristic fragments

arising from the polymeric structures are regularly observed in the mass spectra. In particular, a peak corresponding to the fragment  $[Rh_4]-M-[Rh_4]^+$  is observed in the FAB<sup>+</sup> mass spectra of the compounds 7 (M = Au), 8-9 (M = Ag) and 12 (M = Rh). It is noticeable that all the coordination polymers also exhibit the peaks corresponding to the ions  $[Rh_4]-M^+$  and  $[Rh_4]^+$  which confirm both the integrity of the tetranuclear building blocks and the coordination of the added electrophilic metal fragments.

The solid state structures of the coordination polymers  $[ClCuRh_4(\mu-PyS_2)_2(tfbb)_4]_n$  (6) and  $[ClAuRh_4(\mu-PyS_2)_2(tfbb)_4]_n$  (7) are probably related to that of compound 5 since both have MCl linkers. Possible solid state structures for the cationic coordination polymers containing M<sup>+</sup> (M= Ag and Cu) and Rh(diolefin)<sup>+</sup> linkers are shown in Chart 2 in which the BF<sub>4</sub><sup>-</sup> anions and the auxiliary diolefin ligands have been omitted for clarity. They are based on molecular models assuming linear (d<sup>10</sup>) and square planar (d<sup>8</sup>) coordination environments imposed for the metal linkers. It is noticeable that the suggested zigzag arrangement of the polymeric chains results from the relative disposition of the tetranuclear building blocks in the chains in order to reduce the repulsion between the bulky diolefin ligands.



**Chart 2**. Possible solid state structures for the cationic coordination polymers containing M<sup>+</sup> (M= Ag and Cu) and Rh(diolefin)<sup>+</sup> linkers.

Most of the compounds described herein are insoluble in common organic solvents once they have been isolated as solids that precludes the characterization in solution. The insolubility seems to be a dominant feature of the coordination polymers, and insoluble materials have been proposed to be coordination polymers based on this property.<sup>21</sup> Compounds 10 and 12 are soluble in CDCl<sub>3</sub>. While the <sup>1</sup>H NMR spectrum of **12** was not resolved even at low temperature, that of  $[CuRh_4(\mu PyS_2)_2(cod)_4]_n[BF_4]_n$  (10) was very simple, showing three sharp resonances at  $\delta$  8.18 (d), 7.82(d) and 7.02 (dd) in CDCl<sub>3</sub> at 218 K. A possible interpretation for the simplicity of this spectrum would be the existence of symmetric cyclic oligomers in solution. As shown in Figure 4, a cyclic structure of  $D_2$ symmetry,  $[CuRh_4(\mu-PyS_2)_2(cod)_4]_4^{4+}$ , can be made of four homochiral rhodium tetranuclear complexes, which would account for the observed spectrum, since all the pyridine-2,6-dithiolate bridging ligands become equivalent. Interestingly, the existence of cyclic oligomers and polymeric species made of a given monomeric unit, seems to be controlled by subtle steric and electronic factors.<sup>22</sup> For example, the hydration of the cyclic hexamer  $[{Ag(pymo)}_6]$  gives the polymer  $[{Ag(pymo)}_n] \cdot 2H_2O^{23}$  while the assembling of dinuclear  $[{(CH_2)_n(PPh_2)_2}Au_2]^{2+}$  complexes with the rigid-rod ligand *trans*-1,2-bis(4-pyridyl)ethylene produces gold(I) coordination polymers for n = 3, 4, and rings containing four gold(I) atoms for n = 2.24



**Figure 4**. A possible cyclic structure for  $[CuRh_4(\mu-PyS_2)_2(cod)_4]_n^{n+}$  (**10**) containing four rhodium tetranuclear complexes (n = 4). The cod ligands have been omitted for clarity.

The compounds **5-12** exhibit a weak electric conductivity in the solid state. Room temperature conductivities of pellets made of polycrystalline samples were in the range 1.2-2.8 x  $10^{-7}$  S cm<sup>-1</sup>, while the conductivities found for related rhodium complexes behaving as insulators are less than  $10^{-8}$  S.cm<sup>1</sup>.<sup>25</sup> Interestingly, neither 2,6-dimercaptopyridine nor the tetranuclear complexes [Rh<sub>4</sub>( $\mu$ -PyS<sub>2</sub>)<sub>2</sub>(diolefin)<sub>4</sub>] are conductors under identical experimental conditions.

# Concluding Remarks

The peripheral sulfur atoms in the tetranuclear  $[Rh_4(\mu-PyS_2)_2(diolefin)_4]$  (diolefin = cod, tfbb) complexes have a nucleophilic character, as evidenced the reactions with methyltriflate. Interestingly, the integrity of the tetranuclear framework is sustained upon methylation of the bridging ligands. Both complexes possess two juxtaposed donor sites oriented in a divergent fashion available for coordination of suitable metal ions, and behave as chiral building blocks for the construction of unusual coordination polymers and heteropolynuclear complexes. Finally, it is worth to mention that the related iridium tetranuclear complexes  $[Ir_4(\mu-PyS_2)_2(diolefin)_4]$  (diolefin = cod, tfbb) also have a potential application as ligands. However, although both rhodium and iridium complexes are redox-active species, the iridium complexes are easily oxidized and their behavior as ligands is frequently conditioned by redox processes.

### **Experimental Section**

*General Methods and Starting Materials.* All manipulations were performed under a dry nitrogen atmosphere using Schlenk-tube techniques. Solvents were dried by standard methods and distilled under nitrogen immediately prior to use. The tetranuclear complexes  $[Rh_4(\mu-PyS_2)_2(cod)_4]$  and  $[Rh_4(\mu-PyS_2)_2(tfbb)_4]$  were prepared as described previously.<sup>10</sup> Standard literature procedures were used to prepare CuCl and AgClO<sub>4</sub>.  $[Rh(\mu-Cl)(cod)]_2^{26}$ ,  $[Rh(\mu-Cl)(tfbb)]_2^{27}$ ,  $[AuCl(tht)]^{28}$ ,  $[AuCl(PPh_3)]^{29}$  and  $[Cu(CH_3CN)]_4[BF_4]^{30}$  were prepared according to previously reported methods. AgBF<sub>4</sub> and CF<sub>3</sub>SO<sub>3</sub>Me were purchased from Fluka Chem. and used as received. WARNING: Perchlorate salts are potentially explosive and should only be handle with geat care and in small quantities.

*Physical Measurements.* <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectra were recorded on Varian UNITY and Bruker ARX 300 spectrometers operating at 299.95 and 300.13; 121.42 and 121.49 MHz, respectively. <sup>13</sup>C{<sup>1</sup>H} NMR spectra were recorded on Varian Gemini 300 operating at 75.46 MHz. Chemical shifts are reported in parts per million and referenced to Me<sub>4</sub>Si using the signal of the deuterated solvent (<sup>1</sup>H and <sup>13</sup>C) and 85% H<sub>3</sub>PO<sub>4</sub> (<sup>31</sup>P) as external reference, respectively. IR spectra were recorded on a Perkin-Elmer 783 spectrometer using Nujol mulls between polyethylene sheets or in solution in a cell with NaCl windows. Elemental analysis were performed with a Perkin-Elmer 240-C microanalyzer. Conductivities were measured in *ca.* 5 10<sup>-4</sup> M dichloromethane solutions using a Philips PW 9501/01 conductimeter. Molecular weights were determined with a Knauer osmometer using chloroform solutions of the complexes. Mass spectra were recorded in a VG Autospec double-focusing mass spectrometer operating in the FAB<sup>+</sup> mode. Ions were produced with the standard Cs<sup>+</sup> gun at ca. 30 Kv, 3-nitrobenzyl alcohol (NBA) was used as matrix. Electrical conductivities were measured at room temperature on pellets made of polycrystalline samples by the conventional two-probe method.<sup>31</sup>

## Preparation of the complexes.

[**Rh**<sub>4</sub>(**μ**-**PyS**<sub>2</sub>**Me**)<sub>2</sub>(**cod**)<sub>4</sub>][**CF**<sub>3</sub>**SO**<sub>3</sub>]<sub>2</sub> (1). CF<sub>3</sub>SO<sub>3</sub>Me (21 μL, 0.170 mmol) was added to a solution of [**Rh**<sub>4</sub>(**μ**-**PyS**<sub>2</sub>)<sub>2</sub>(cod)<sub>4</sub>] (0.100 g, 0.088 mmol) in dichloromethane (10 mL) to give a dark red solution. Concentration of this solution to *ca*. 5 mL and further addition of methanol (5 mL) gave a dark solid, which was removed by filtration through celite. Concentration of the resulting red solution to *ca*. 1 mL and addition of methanol rendered the complex as a red microcrystalline solid, which was filtered, washed with metanol and dried under vacuum. Yield: 0.107 g (84%). Anal. Calcd for C<sub>46</sub>H<sub>60</sub>F<sub>6</sub>N<sub>2</sub>O<sub>6</sub>Rh<sub>4</sub>S<sub>6</sub>: C, 37.97; H, 4.16; N, 1.93. Found: C, 37.60; H, 3.74; N, 1.92. MS (FAB<sup>+</sup>, CH<sub>2</sub>Cl<sub>2</sub>, m/z): 1141 ([Rh<sub>4</sub>(PyS<sub>2</sub>Me)(PyS<sub>2</sub>)(cod)<sub>4</sub>]<sup>+</sup>, 4%), 945 ([Rh<sub>3</sub>(PyS<sub>2</sub>Me)<sub>2</sub>(cod)<sub>3</sub>]<sup>+</sup>, 58%), 578 ([Rh<sub>2</sub>(PyS<sub>2</sub>Me)(cod)<sub>2</sub>]<sup>+</sup>, 100%). Λ<sub>M</sub> (S.cm<sup>2</sup>.mol<sup>-1</sup>): 157 (acetone, 4.94 10<sup>-4</sup> M). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 298 K) δ: 8.39 (d, 2H, J<sub>H-H</sub> = 7.8 Hz), 7.53 (dd, 2H), 7.11 (d, 2H, J<sub>H-H</sub> = 8.2 Hz) (PyS<sub>2</sub>Me ligands), 5.26 (m, 2H, =CH), 5.03 (m, 2H, =CH), 4.90 (m, 4H, =CH), 4.52 (m, 2H, =CH), 4.40 (m, 2H, =CH), 4.00

(m, 2H, =CH), 3.41 (m, 2H, =CH) (cod ligands), 2.80 (s, 6H, PyS<sub>2</sub><u>Me</u>), 3.0-1.5 (several m, 32H, >CH<sub>2</sub>) (cod ligands). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 298 K)  $\delta$ : 167.0, 156.0, 140.2, 130.4, 121.0 (PyS<sub>2</sub>Me ligands), 92.2 (d, J<sub>Rh-C</sub> = 11 Hz), 90.4 (d, J<sub>Rh-C</sub> = 13 Hz), 88.1 (d, J<sub>Rh-C</sub> = 11 Hz), 87.9 (d, J<sub>Rh-C</sub> = 11 Hz), 87.0 (d, J<sub>Rh-C</sub> = 11 Hz), 86.9 (d, J<sub>Rh-C</sub> = 12 Hz), 86.5 (d, J<sub>Rh-C</sub> = 12 Hz), 79.7 (d, J<sub>Rh-C</sub> = 11.5 Hz) (=CH, cod ligands), 34.9, 34.0, 33.0, 32.5, 29.2, 29.1, 28.4, 27.5 (>CH, cod ligands), 17.9 (s, PyS<sub>2</sub><u>Me</u>).

 $[Rh_4(\mu-PyS_2)(\mu-PyS_2Me)(tfbb)_4][CF_3SO_3]$  (2). CF\_3SO\_3Me (5.70 µL, 0.047 mmol) was added to a solution of [Rh<sub>4</sub>(PyS<sub>2</sub>)<sub>2</sub>(tfbb)<sub>4</sub>] (0.075 g, 0.047 mmol) in dichloromethane (10 mL) to give a violet solution which was stirred for 2 hours. Concentration of the solution to ca. 1 mL and addition of hexane gave the complex as a dark red microcrystalline solid, which was filtered, washed with hexane and dried under vacuum. Yield: 0.075 g (90%). Anal. Calcd for  $C_{60}H_{33}F_{19}N_2O_3Rh_4S_5$ : C, 40.88; H, 1.88; N. 1.59. Found: C, 40.82; H, 1.80; N, 1.62. MS (FAB+, CH<sub>2</sub>Cl<sub>2</sub>, m/z): 1613  $([Rh_4(PyS_2Me)(PyS_2)(tfbb)_4]^+,$ 100%), 1284  $([Rh_3(PyS_2Me)(PyS_2)(tfbb)_3]^+,$ 25%), 814 ([Rh<sub>2</sub>(PyS<sub>2</sub>Me)(tfbb)<sub>2</sub>]<sup>+</sup>, 100%). A<sub>M</sub> (S.cm<sup>2</sup>.mol<sup>-1</sup>): 144 (acetone, 5.55 10<sup>-4</sup> M). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 298 K) δ: 8.27 (d, 1H, J<sub>H-H</sub> = 7.3 Hz), 7.06 (dd, 1H), 7.00 (br, 1H) (PyS<sub>2</sub> ligand), 8.01 (d, 1H, J<sub>H-H</sub> = 7.3 Hz), 7.26 (dd, 1H), , 6.86 (d, 1H,  $J_{H-H} = 8.0$  Hz) (PyS<sub>2</sub>Me ligand), 6.17 (m, 1H, CH), 6.10 (m, 1H, CH), 5.96 (m, 1H, CH), 5.83 (m, 3H, CH), 5.69 (m, 2H, CH), 5.42 (m, 1H, =CH), 4.86 (m, 2H, =CH), 4.72 (m, 1H, =CH), 4.58 (m, 1H, =CH), 4.51 (m, 3H, =CH), 4.37 (m, 5H, =CH), 4.23 (m, 1H, =CH), 4.17 (m, 1H, =CH), 3.99 (m, 1H, =CH) (tfbb ligands), 2.79 (s, 3H, PyS<sub>2</sub>Me ligand). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 298 K) δ: 170.2, 167.4, 162.8, 152.3, 138.6, 137.6, 128.2, 125.7, 122.9, 118.3 (PyS<sub>2</sub>Me and PyS<sub>2</sub>) ligands), 140.0 (dm,  $J_{F-C} = 260$  Hz), 138.0 (dm,  $J_{F-C} = 265$  Hz), 127.5-125.8 (m) (C-F, tfbb ligands) 68.5 (m), 64.8 (m), 62.6 (m), 61.8 (m), 59.9 (m), 58.3 (m), 55.0 (m), 54.5 (m), 49.9 (m), 41.2 (m), 39.9 (m), (=CH, tfbb ligands), 39.8-39.3 (m) (CH, tfbb ligands) 17.6 (s, PyS<sub>2</sub>Me).

 $[(PPh_3)_2Au_2Rh_4(\mu-PyS_2)_2(cod)_4][ClO_4]_2$  (3). Solid AgClO<sub>4</sub> (0.027 g, 0.133 mmol) was added to a solution of  $[AuCl(PPh_3)]$  (0.066 g, 0.133 mmol) in acetone (5 mL) to give a white suspension which was stirred for 30 min. in the dark. Silver chloride was removed by filtration through celite and the

resulting solution was reacted with a solution of  $[Rh_4(\mu-PyS_2)_2(cod)_4]$  (0.075 g, 0.066 mmol) in dichloromethane (10 mL) for one hour. Concentration of the dark red solution to *ca.* 1 mL and addition of methanol (10 mL) and diethyl ether (5 mL) gave the complex as a red microcrystalline solid, which was filtered off, washed with cold methanol and vacuum dried. Yield: 0.111 g (75%). Anal. Calcd for C<sub>78</sub>H<sub>84</sub>Au<sub>2</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>8</sub>P<sub>2</sub>Rh<sub>4</sub>S<sub>4</sub>: C, 41.75; H, 3.77; N, 1.25. Found: C, 41.60; H, 3.90; N, 1.21. MS (FAB<sup>+</sup>, CH<sub>2</sub>Cl<sub>2</sub>, m/z): 1585 ([Rh<sub>4</sub>]-Au(PPh<sub>3</sub>)<sup>+</sup>, 100%), 1126 ([Rh<sub>4</sub>]<sup>+</sup>, 28%).  $\Lambda_M$  (S.cm<sup>2</sup>.mol<sup>-1</sup>): 200 (acetone, 3.72 10<sup>-4</sup> M). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 293 K)  $\delta$ : 8.20 (d, 2H, J<sub>H-H</sub> = 7.8 Hz, PyS<sub>2</sub>), 7.60 (m, 18H, PPh<sub>3</sub>), 7.46 (m, 14H, PPh<sub>3</sub> and PyS<sub>2</sub>), 7.32 (t, 2H, J<sub>H-H</sub> = 7.8 Hz, PyS<sub>2</sub>), 5.15 (m, 2H, =CH), 4.90 (m, 4H, =CH), 4.70 (m, 4H, =CH), 4.15 (m, 2H, =CH), 4.05 (m, 4H, =CH), 3.30 (m, 2H, >CH<sub>2</sub>), 3.00-2.60 (m, 6H, >CH<sub>2</sub>), 2.65-2.00 (m, 16H, >CH<sub>2</sub>), 1.90-1.50 (m, 8H, >CH<sub>2</sub>) (cod ligands). <sup>31</sup>P NMR (CDCl<sub>3</sub>, 293 K)  $\delta$ : 36.0 (s).

[(PPh<sub>3</sub>)<sub>2</sub>Au<sub>2</sub>Rh<sub>4</sub>(μ-PyS<sub>2</sub>)<sub>2</sub>(tfbb)<sub>4</sub>][ClO<sub>4</sub>]<sub>2</sub> (4). An acetone solution of [Au(PPh<sub>3</sub>)(Me<sub>2</sub>CO)][ClO<sub>4</sub>] (0.094 mmol), prepared "in situ" as described above, was reacted with [Rh<sub>4</sub>(μ-PyS<sub>2</sub>)<sub>2</sub>(tfbb)<sub>4</sub>] (0.075 g, 0.047 mmol) in dichloromethane (10 mL) to give a dark solution. The complex was isolated as dark violet microcrystals by concentration of the solution and addition of methanol (10 mL). Yield: 0.092 g (72%). Anal. Calcd for C<sub>94</sub>H<sub>60</sub>Au<sub>2</sub>Cl<sub>2</sub>F<sub>16</sub>N<sub>2</sub>O<sub>8</sub>P<sub>2</sub>Rh<sub>4</sub>S<sub>4</sub>: C, 43.15; H, 2.31; N, 1.07. Found: C, 43.00; H, 2.40; N, 1.07. MS (FAB<sup>+</sup>, CH<sub>2</sub>Cl<sub>2</sub>, m/z): 2058 ([Rh<sub>4</sub>]-Au(PPh<sub>3</sub>)<sup>+</sup>, 100%), 1598 ([Rh<sub>4</sub>]<sup>+</sup>, 23%). Λ<sub>M</sub> (S.cm<sup>2</sup>.mol<sup>-1</sup>): 178 (acetone, 3.98 10<sup>-4</sup> M). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 218 K) δ: 8.29 (d, 2H, J<sub>H-H</sub> = 7.5 Hz, PyS<sub>2</sub>), 7.8-7.4 (m, 30H, PPh<sub>3</sub>), 7.14 (d, 2H, J<sub>H-H</sub> = 7.7 Hz, PyS<sub>2</sub>), 6.89 (dd, 2H, PyS<sub>2</sub>), 5.86 (m, 2H, CH), 5.70 (m, 4H, CH), 5.35 (m, 4H, =CH), 5.30 (m, 2H, CH), 4.66 (m, 4H, =CH), 4.56 (m, 2H, =CH), 4.36 (m, 2H, =CH), 4.13 (m, 2H, =CH), 3.96 (m, 2H, =CH), (tfbb ligands). <sup>31</sup>P NMR (CDCl<sub>3</sub>, 218 K) δ: 36.6 (s).

[ClCuRh<sub>4</sub>( $\mu$ -PyS<sub>2</sub>)<sub>2</sub>(cod)<sub>4</sub>]<sub>n</sub> (5). Solid CuCl (0.066 g, 0.132 mmol) was added to a solution of [Rh<sub>4</sub>( $\mu$ -PyS<sub>2</sub>)<sub>2</sub>(cod)<sub>4</sub>] (0.075g, 0.066 mmol) in dichloromethane (15 mL) and stirred for 3 h. The resulting dark red solution was filtered through celite and then concentrated under vacuum to *ca*. 1 mL.

Slow addition of diethyl ether (10 mL) gave an orange solid which was filtered off, washed with diethyl ether and dried under vacuum. Yield: 0.059 g (80%). Anal. Calcd for  $C_{42}H_{54}ClCuN_2Rh_4S_4$ : C, 41.15; H, 4.44; N, 2.28. Found: C, 41.02; H, 4.73; N, 2.26. MS (FAB<sup>+</sup>, CH<sub>2</sub>Cl<sub>2</sub>, m/z): 1289 (ClCu<sub>2</sub>-[Rh<sub>4</sub>]<sup>+</sup>, 5%), 1227 (ClCu-[Rh<sub>4</sub>]<sup>+</sup>, 12%), 1189 (Cu-[Rh<sub>4</sub>]<sup>+</sup>, 25%), 1126 ([Rh<sub>4</sub>]<sup>+</sup>, 81%). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 293 K, aromatic region)  $\delta$ : 8.40 (d, 2H), 7.90 (d, 2H), 6.90 (m, 4H), 6.80 (d, 2H), 6.55 (d, 2H), 6.40 (m, 2H), 6.30 (t, 2H), 6.05 (t) (PyS<sub>2</sub>). Mol. Weight. Found: 1730.

[ClCuRh<sub>4</sub>( $\mu$ -PyS<sub>2</sub>)<sub>2</sub>(tfbb)<sub>4</sub>]<sub>n</sub> (6). Solid CuCl (0.062 g, 0.062 mmol) was reacted with [Rh<sub>4</sub>( $\mu$ -PyS<sub>2</sub>)<sub>2</sub>(tfbb)<sub>4</sub>] (0.100 g, 0.062 mmol) in dichloromethane (15 mL) to give a purple suspension in three hours. Concentration under vacuum and addition of methanol gave the complex as a purple solid, which was filtered, washed with methanol and dried under vacuum. Yield: 0.082 g (77%). Anal. Calcd for C<sub>58</sub>H<sub>30</sub>ClCuF<sub>16</sub>N<sub>2</sub>Rh<sub>4</sub>S<sub>4</sub>: C, 41.03; H, 1.78; N, 1.65. Found: C, 40.92; H, 1.75; N, 1.62. MS (FAB<sup>+</sup>, CH<sub>2</sub>Cl<sub>2</sub>, m/z): 1662 (Cu-[Rh<sub>4</sub>]<sup>+</sup>, 5%), 1597 ([Rh<sub>4</sub>]<sup>+</sup>, 100%).

[ClAuRh<sub>4</sub>( $\mu$ -PyS<sub>2</sub>)<sub>2</sub>(tfbb)<sub>4</sub>]<sub>n</sub> (7). Solid [AuCl(tht)] (0.020 g, 0.062 mmol) was added to a solution of [Rh<sub>4</sub>( $\mu$ -PyS<sub>2</sub>)<sub>2</sub>(tfbb)<sub>4</sub>] (0.100 g, 0.062 mmol) in dichloromethane (10 mL) to give a dark purple solution in two hours. Concentration of the solution to *ca*. 1 mL and slow addition of diethyl ether (10 mL) gave the complex as a purple microcrystalline solid which was filtered, washed with diethyl ether and acetone and dried under vacuum. Yield: 0.090 g (79%). Anal. Calcd for C<sub>58</sub>H<sub>30</sub>ClAuF<sub>16</sub>N<sub>2</sub>Rh<sub>4</sub>S<sub>4</sub>: C, 38.04; H, 1.65; N, 1.53. Found: C, 38.03; H, 1.59; N, 1.52. MS (FAB<sup>+</sup>, CH<sub>2</sub>Cl<sub>2</sub>, m/z): 3392 (Au-[Rh<sub>4</sub>]<sub>2</sub><sup>+</sup>, 60%), 1795 (Au-[Rh<sub>4</sub>]<sup>+</sup>, 10%), 1598 ([Rh<sub>4</sub>]<sup>+</sup>, 100%).

 $[AgRh_4(\mu-PyS_2)_2(cod)_4]_n[BF_4]_n$  (8). A solution of AgBF<sub>4</sub> (0.018 g, 0.095 mmol) in acetone (5 mL) was added to a solution of  $[Rh_4(\mu-PyS_2)_2(cod)_4]$  (0.107 g, 0.095 mmol) in dichloromethane (15 mL). The dark red mixture was stirred for one h and then concentrated under vacuum to *ca*. 1 mL. Addition of diethyl ether (10 mL) gave the complex as a dark red solid which was filtered off, washed with diethyl ether and acetone, and dried under vacuum. Yield: 0.106 g (84%). Anal. Calcd for C<sub>42</sub>H<sub>54</sub>AgBF<sub>4</sub>N<sub>2</sub>Rh<sub>4</sub>S<sub>4</sub>: C, 38.17; H, 4.12; N, 2.12. Found: C, 38.05; H, 3.92; N, 2.10. MS (FAB<sup>+</sup>,

CH<sub>2</sub>Cl<sub>2</sub>, m/z): 2361 (Ag-[Rh<sub>4</sub>]<sub>2</sub><sup>+</sup>, 10%), 1235 (Ag-[Rh<sub>4</sub>]<sup>+</sup>, 80%), 1126 ([Rh<sub>4</sub>]<sup>+</sup>, 100%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 218 K, aromatic region) δ: 8.70 (m), 8.08 (m), 7.96 (m), 7.88 (m), 7.70 (m), 7.64 (m), 7.54 (m), 7.10 (m), 6.80 (m), 6.62 (m), 6.46 (m) (PyS<sub>2</sub> ligands).

[AgRh<sub>4</sub>( $\mu$ -PyS<sub>2</sub>)<sub>2</sub>(tfbb)<sub>4</sub>]<sub>n</sub>[BF<sub>4</sub>]<sub>n</sub> (9). The compound was prepared from [Rh<sub>4</sub>( $\mu$ -PyS<sub>2</sub>)<sub>2</sub>(tfbb)<sub>4</sub>] (0.102 g, 0.064 mmol) and AgBF<sub>4</sub> (0.012 g, 0.064 mmol) following the procedure described above. The complex crystallized out in dichloromethane and was isolated as a purple solid after concentration and addition of methanol (10 mL). Yield: 0.105 g (91%). Anal. Calcd for C<sub>58</sub>H<sub>30</sub>AgBF<sub>20</sub>N<sub>2</sub>Rh<sub>4</sub>S<sub>4</sub>: C, 38.84; H, 1.69; N, 1.56. Found: C, 38.68; H, 1.68; N, 1.57. MS (FAB<sup>+</sup>, CH<sub>2</sub>Cl<sub>2</sub>, m/z): 3304 (Ag-[Rh<sub>4</sub>]<sub>2</sub><sup>+</sup>, 10%), 1706 (Ag-[Rh<sub>4</sub>]<sup>+</sup>, 35%), 1598 ([Rh<sub>4</sub>]<sup>+</sup>, 100%).

[CuRh<sub>4</sub>(μ-PyS<sub>2</sub>)<sub>2</sub>(cod)<sub>4</sub>]<sub>n</sub>[BF<sub>4</sub>]<sub>n</sub> (10). [Cu(CH<sub>3</sub>CN)]<sub>4</sub>[BF<sub>4</sub>] (0.022 g, 0.070 mmol) was added to a solution of [Rh<sub>4</sub>(μ-PyS<sub>2</sub>)<sub>2</sub>(cod)<sub>4</sub>] (0.075 g, 0.066 mmol) in dichloromethane (10 mL). The dark red mixture was stirred for two hours and then filtered through celite. Concentration under vacuum to *ca*. 1 mL and addition of diethyl ether (5 mL) and methanol (5 mL) gave the complex as a dark red solid which was filtered off, washed with methanol and acetone, and dried under vacuum. Yield: 0.071 g (84%). Anal. Calcd for C<sub>42</sub>H<sub>54</sub>BCuF<sub>4</sub>N<sub>2</sub>Rh<sub>4</sub>S<sub>4</sub>: C, 39.50; H, 4.26; N, 2.19. Found: C, 39.30; H, 4.10; N, 2.14. MS (FAB\*, CH<sub>2</sub>Cl<sub>2</sub>, m/z): 1189 (Cu-[Rh<sub>4</sub>]<sup>+</sup>, 10%), 1126 ([Rh<sub>4</sub>]<sup>+</sup>, 65%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 218 K, aromatic region) δ: 8.18 (d, J<sub>H-H</sub> = 7.8 Hz), 7.82 (d, J<sub>H-H</sub> = 7.8 Hz), 7.02 (dd) (PyS<sub>2</sub>).

[CuRh<sub>4</sub>( $\mu$ -PyS<sub>2</sub>)<sub>2</sub>(tfbb)<sub>4</sub>]<sub>n</sub>[BF<sub>4</sub>]<sub>n</sub> (11). The compound was prepared from [Rh<sub>4</sub>( $\mu$ -PyS<sub>2</sub>)<sub>2</sub>(tfbb)<sub>4</sub>] (0.075 g, 0.047 mmol) and [Cu(CH<sub>3</sub>CN)]<sub>4</sub>[BF<sub>4</sub>] (0.010 g, 0.047 mmol) following the procedure described above. The complex crystallized out in dichloromethane and was isolated as a purple garnet solid after concentration of the solution followed by addition of methanol (10 mL). Yield: 0.065 g (79%). Anal. Calcd for C<sub>58</sub>H<sub>30</sub>BCuF<sub>20</sub>N<sub>2</sub>Rh<sub>4</sub>S<sub>4</sub>: C, 39.83; H, 1.73; N, 1.60. Found: C, 39.63; H, 1.59; N, 1.59. MS (FAB<sup>+</sup>, CH<sub>2</sub>Cl<sub>2</sub>, m/z): 1660 (Cu-[Rh<sub>4</sub>]<sup>+</sup>, 20%), 1598 ([Rh<sub>4</sub>]<sup>+</sup>, 100%).

 $[\mathbf{Rh}_5(\mu-\mathbf{PyS}_2)_2(\mathbf{cod})_5]_n[\mathbf{BF}_4]_n$  (12). Solid AgBF<sub>4</sub> (0.035 g, 0.1775 mmol) was added to a solution of  $[\mathbf{Rh}(\mu-\mathbf{Cl})(\mathbf{cod})]_2$  (0.044 g, 0.088 mmol) in acetone (5 mL). The silver chloride was removed by

filtration through celite and the solution containing the solvated species  $[Rh(cod)(Me_2CO)_2][BF_4]$  was transferred to a solution of  $[Rh_4(\mu-PyS_2)_2(cod)_4]$  (0.100 g, 0.088 mmol) in dichloromethane (15 mL). The resulting violet solution was stirred for 1 h and then concentrated under vacuum to *ca.* 1 mL. Slow addition of diethyl ether gave the complex as a violet microcrystalline solid which was filtered, washed with diethyl ether, and dried under vacuum. Yield: 0.114 g (90%). Anal. Calcd for  $C_{50}H_{66}BF_4N_2Rh_5S_4$ : C, 42.17; H, 4.67; N, 1.97. Found: C, 42.04; H, 4.44; N, 1.91. MS (FAB<sup>+</sup>, CH<sub>2</sub>Cl<sub>2</sub>, m/z): 2464 ([Rh<sub>4</sub>]<sub>2</sub>-Rh(cod)<sup>+</sup>, 7%), 1337 ([Rh<sub>4</sub>]-Rh(cod)<sup>+</sup>, 47%), 1229 ([Rh<sub>4</sub>]-Rh<sup>+</sup>, 16%), 1126 ([Rh<sub>4</sub>]<sup>+</sup>, 100%).  $\Lambda_M$  (S.cm<sup>2</sup>.mol<sup>-1</sup>): 84 (acetone, 5.57 10<sup>-4</sup> M).

[**Rh**<sub>5</sub>( $\mu$ -**PyS**<sub>2</sub>)<sub>2</sub>(**tfbb**)<sub>5</sub>]<sub>n</sub>[**BF**<sub>4</sub>]<sub>n</sub> (13). An acetone solution (5 mL) of [Rh(tfbb)(Me<sub>2</sub>CO)<sub>2</sub>][**B**F<sub>4</sub>] (0.054 mmol), prepared as describe above from [Rh( $\mu$ -Cl)(tfbb)]<sub>2</sub> and AgBF<sub>4</sub>, was added to a solution of [Rh<sub>4</sub>( $\mu$ -PyS<sub>2</sub>)<sub>2</sub>(tfbb)<sub>4</sub>] (0.087 g, 0.054 mmol) in dichloromethane (15 mL) to give a deep violet solution in 1 h. Concentration of the solution under vacuum to *ca.* 2 mL and addition of methanol gave the complex as a violet solid which was filtered, washed with methanol and dried under vacuum. Yield: 0.115 g (94%). Anal. Calcd for C<sub>70</sub>H<sub>36</sub>BF<sub>4</sub>N<sub>2</sub>Rh<sub>5</sub>S<sub>4</sub>: C, 41.73; H, 1.80; N, 1.39. Found: C, 41.53; H, 1.78; N, 1.39. MS (FAB<sup>+</sup>, CH<sub>2</sub>Cl<sub>2</sub>, m/z): 1927 ([Rh<sub>4</sub>]-Rh(tfbb)<sup>+</sup>, 65%), 1701 ([Rh<sub>4</sub>]-Rh<sup>+</sup>, 7%), 1598 ([Rh<sub>4</sub>]<sup>+</sup>, 100%).

Structural Determination of Complex 4. A summary of crystal data and refinement parameters for the structural analysis is given in Table 2. Suitable crystals for the X-ray diffraction study were obtained by slow diffusion of hexane into a concentrated solution of 4 in a dichloromethane/acetone mixture. A dark violet irregular shaped crystal (0.28 x 0.14 x 0.12 mm) of 4 was glued to a glass fiber and mounted on Bruker SMART APEX diffractometer. The instrument was equipped with CCD area detector and data were collected using graphite-monochromated Mo K $\alpha$  radiation ( $\lambda$ = 0.71073 Å) at low temperature (100 K). Cell constants were obtained from the least-squares refinement of three-dimensional centroids of 5264 reflections ( $4.9 \le 20 \le 42.3^{\circ}$ ). Data were measured (59718 ref. ( $1.9 \le 0 \le 25.1^{\circ}$ ); 19583 unique,  $R_{int}$ = 0.0932) through the use of CCD recording of narrow  $\omega$  rotation frames ( $0.3^{\circ}$  each) and were integrated with the Bruker SAINT program which includes Lorentz and polarization corrections.<sup>32</sup> Absorption correction was applied by using the SADABS routine (min. max. transmission factors 0.533 and 0.645).<sup>33</sup>

The structure was easily solved by Patterson methods, completed by subsequent difference Fourier techniques and refined by full-matrix least-squares on  $F^2$  (SHELXL-97)<sup>34</sup> with initial isotropic thermal parameters. After anisotropic refinement of all the atoms of the polynuclear cationic metal complex, several electron residuals were detected spread in the cell localized in quite a few spatial regions. At this stage, the perchlorate anions were straightforwardly found, but one of them exhibits static disorder for three oxygen atoms (O(6), O(7) and O(8)). Two solvation disordered CH<sub>2</sub>Cl<sub>2</sub> molecules were also identified in the subsequent difference Fourier maps; both of them need a disorder modelation from two overlapping dichloromethane molecules. A third acetone solvation molecule was also recognized among the numerous electron residuals. All the atoms involved in disorder (one perchlorate, two CH<sub>2</sub>Cl<sub>2</sub> and the acetone molecule) were refined as isotropic atoms and maintained under geometric restrictions during refinement. Hydrogen atoms were included in calculated positions for the hexanuclear cation; their positional and displacement parameters were incorporated in the least-squares refinement riding on carbon atoms.

At this step, several residuals of significant electron density (3-4  $e^{-/A^3}$ ) were still present in the difference Fourier map; they did not display significant short contacts to any of the already identified and refined atoms. Several attempts to model this electron density were carried out considering the different solvent molecules used in the crystallization process. Unfortunately no clear disorder model could be established. As an alternative, an evaluation of potential solvent regions showed the presence of four voids in the cell, completing an approximate volume of 1878 Å<sup>3</sup>; an electron count over this volume provided an estimate of 216 e<sup>-</sup> per region (a total of 866 e<sup>-</sup> in the cell).<sup>35</sup> Bearing in mind the solvents used in the crystallization, we interpreted these figures assuming the presence of four highly disordered hexane molecules (4 x 50 e<sup>-</sup>/hexane mol.) in each of these four 'solvent regions' to

the total structure factors was calculated *via* discrete Fourier transformation and incorporated in the final least-squares refinement of the ordered part of the structure.<sup>36</sup> Data presented in Table 2 assumes the presence of the four hexane molecules in the independent part of the cell in addition to the previously identified moieties (the polynuclear cation, two anions, dichloromethane and acetone). Atomic scattering factors were used as implemented in the program.<sup>34</sup>

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**Supporting Information Available.** An X-ray crystallographic file, in CIF format, containing full details of the structural analysis of **4** and the observed, and calculated fine structure of the molecular fragments  $Ag-[Rh_4]_2^+$  and  $Ag-[Rh_4]^+$  detected in the in the mass spectrum **8**. This material is available free of charge via Internet at http://pubs.acs.org.

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Rh(1)-S(1)	2.366(3)	Rh(4)-S(4)	2.380(3)
Rh(1)-S(3)	2.370(3)	Rh(4)-S(2)	2.374(3)
Rh(1)-C(11)	2.120(11)	Rh(4)-C(29)	2.133(12)
Rh(1)-C(12)	2.126(11)	Rh(4)-C(30)	2.110(10)
Rh(1)-C(14)	2.176(10)	Rh(4)-C(32)	2.129(10)
Rh(1)-C(15)	2.145(10)	Rh(4)-C(33)	2.199(10)
Rh(2)-S(1)	2.358(3)	Rh(3)-S(4)	2.363(3)
Rh(2)-N(1)	2.113(8)	Rh(3)-N(2)	2.115(8)
Rh(2)-C(17)	2.156(10)	Rh(3)-C(26)	2.157(10)
Rh(2)-C(18)	2.158(10)	Rh(3)-C(27)	2.107(9)
Rh(2)-C(20)	2.133(10)	Rh(3)-C(23)	2.123(10)
Rh(2)-C(21)	2.137(10)	Rh(3)-C(24)	2.145(10)
Au(1)-S(3)	2.328(3)	Au(2)-S(2)	2.330(3)
Au(1)-P(1)	2.254(3)	Au(2)-P(2)	2.247(3)
S(1)-C(10)	1.757(10)	S(4)-C(5)	1.790(10)
S(3)-C(1)	1.752(11)	S(2)-C(6)	1.774(11)
N(1)-C(1)	1.365(11)	N(2)-C(6)	1.362(12)
N(1)-C(5)	1.344(12)	N(2)-C(10)	1.364(12)
C(1)-C(2)	1.334(13)	C(6)-C(7)	1.359(13)
C(2)-C(3)	1.377(13)	C(7)-C(8)	1.422(13)
C(3)-C(4)	1.375(12)	C(8)-C(9)	1.404(13)
C(4)-C(5)	1.374(13)	C(9)-C(10)	1.382(13)
C(11)-C(12)	1.345(13)	C(29)-C(30)	1.413(14)
C(14)-C(15)	1.345(13)	C(32)-C(33)	1.366(15)
C(17)-C(18)	1.402(13)	C(26)-C(27)	1.376(13)
C(20)-C(21)	1.397(13)	C(23)-C(24)	1.360(13)

S(1)-Rh(1)-S(3)	102.36(11)	S(4)-Rh(4)-S(2)	101.17(10)
S(1)-Rh(1)-M(1)	91.4(2)	S(4)-Rh(4)-M(7)	94.3(3)

S(1)-Rh(1)-M(2)	158.1(3)	S(4)-Rh(4)-M(8)	159.9(3)
S(3)-Rh(1)-M(1)	165.7(3)	S(2)-Rh(4)-M(7)	164.2(3)
S(3)-Rh(1)-M(2)	97.1(3)	S(2)-Rh(4)-M(8)	96.0(3)
M(1)-Rh(1)-M(2)	70.1(4)	M(7)-Rh(4)-M(8)	69.5(4)
S(1)-Rh(2)-N(1)	90.2(2)	S(4)-Rh(3)-N(2)	89.8(3)
S(1)-Rh(2)-M(3)	101.5(2)	S(4)-Rh(3)-M(6)	102.0(2)
S(1)-Rh(2)-M(4)	167.3(2)	S(4)-Rh(3)-M(5)	169.5(2)
N(1)-Rh(2)-M(3)	168.3(3)	N(2)-Rh(3)-M(6)	165.4(3)
N(1)-Rh(2)-M(4)	97.8(3)	N(2)-Rh(3)-M(5)	97.6(3)
M(3)-Rh(2)-M(4)	70.5(3)	M(5)-Rh(3)-M(6)	69.6(3)
S(3)-Au(1)-P(1)	177.04(12)	S(2)-Au(2)-P(2)	175.86(11)
Rh(1)-S(1)-Rh(2)	81.12(9)	Rh(4)-S(4)-Rh(3)	83.42(9)
Rh(1)-S(1)-C(10)	111.2(3)	Rh(4)-S(4)-C(5)	111.9(4)
Rh(2)-S(1)-C(10)	107.8(4)	Rh(3)-S(4)-C(5)	106.3(4)
Rh(1)-S(3)-Au(1)	82.59(10)	Rh(4)-S(2)-Au(2)	81.25(10)
Rh(1)-S(3)-C(1)	114.5(4)	Rh(4)-S(2)-C(6)	115.3(4)
Au(1)-S(3)-C(1)	98.4(4)	Au(2)-S(2)-C(6)	98.7(4)
Rh(2)-N(1)-C(1)	118.8(7)	Rh(3)-N(2)-C(6)	120.1(7)
Rh(2)-N(1)-C(5)	122.5(7)	Rh(3)-N(2)-C(10)	120.7(7)
C(1)-N(1)-C(5)	118.7(9)	C(6)-N(2)-C(10)	119.2(9)

 $^{*}M(1)$  to M(8) represent the midpoints of the olefinic bonds coordinated to Rh atoms.

 $C_{94}H_{60}Au_2Cl_2F_{16}N_2O_8P_2Rh_4S_4 \cdot 2 CH_2Cl_2 \cdot C_3H_6O \cdot 4 C_6H_{14}$ empirical formula 3288.71 fw space group  $P2_1/n$  (No. 14) *a*, Å 22.7939(12) b, Å 21.9335(11) *c*, Å 24.5094(12) β, ° 115.2690(10) *V*, Å<sup>3</sup> 11081.0(10) 4 Ζ  $D_{\text{calcd}}, \text{g·cm}^{-3}$  1.971  $\mu$ , mm<sup>-1</sup> 3.560 no data/restraints/param 19583/159/1271 *GOF*(all data)<sup>a</sup>0.832  $R_{l}(F) (F^{2} \epsilon 2\sigma(F^{2}))^{b} = 0.0548$  $wR_2(F^2)$  (all data)<sup>c</sup> 0.1111

<sup>a</sup> GOF =  $(\Sigma[w(F_0^2 - F_c^2)^2] / (n - p))^{1/2}$ , where n and p are the number of data and parameters. <sup>b</sup> $R_I(F) = \Sigma ||F_0| - |F_c|| / \Sigma |F_0|$  for 10069 observed reflections. <sup>c</sup> $wR_2(F^2) = (\Sigma[w(F_0^2 - F_c^2)^2] / \Sigma[w(F_0^2)^2])^{1/2}$  where  $w = 1/[\sigma^2(F_0^2) + (aP)^2]$  and  $P = [\max(0, F_0^2) + 2F_c^2]/3$ .

Tetranuclear [Rh<sub>4</sub>(µ-PyS<sub>2</sub>)<sub>2</sub>(diolefin)<sub>4</sub>] Complexes as Building Blocks for New Inorganic Architectures: Synthesis of Coordination Polymers and Heteropolynuclear Complexes with Electrophilic d<sup>8</sup> and d<sup>10</sup> Metal Fragments

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The tetranuclear complexes  $[Rh_4(\mu-PyS_2)_2(diolefin)_4]$  possess two donor sites at the peripheral sulfur atoms prone to bind suitable metal centres. From them, discrete heterometallic complexes and infinite one-dimensional chains may be assembled in a stereoselective way by using the appropriate metal fragments.

