Bis(hydrosulfido)-bridged dinuclear rhodium(I) complexes as a platform for the synthesis of trinuclear sulfido aggregates with the core $[\text{MRh}_2(\mu_3\text{-S}_2)]$ ($\text{M} = \text{Rh}, \text{Ir}, \text{Pd}, \text{Pt}, \text{Ru}$)

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Reaction of $[\text{Rh}(\mu\text{-SH})(\text{CO})(\text{PPh}_3)_2]$ or $[\text{Rh}(\mu\text{-SH})\{\text{P}(\text{O}i\text{Pr})_3\}_2]$ with $[\text{Cp}^*\text{MCl}_2]$ ($\text{M} = \text{Rh}, \text{Ir}$) in the presence of NEt_3 afforded the Rh_3 and IrRh_2 sulfido-bridged compounds $[\text{Cp}^*\text{M}(\mu_3\text{-S})_2\text{Rh}_2(\text{CO})_2(\text{PPh}_3)_2]$ ($\text{M} = \text{Rh}$, **1**; Ir , **2**) and $[\text{Cp}^*\text{Rh}(\mu_3\text{-S})_2\text{Rh}_2\{\text{P}(\text{O}i\text{Pr})_3\}_4]$ (**3**). Reaction with $[\text{MCl}_2(\text{cod})]$ ($\text{M} = \text{Pd}, \text{Pt}$), *cis*- $[\text{PtCl}_2(\text{PPh}_3)_2]$ or $[(\eta^6\text{-C}_6\text{H}_6)\text{RuCl}_2]$ under the same experimental conditions gave $[(\text{cod})\text{M}(\mu_3\text{-S})_2\text{Rh}_2\{\text{P}(\text{O}i\text{Pr})_3\}_4]$ ($\text{M} = \text{Pd}$, **6**; Pt , **7**), $[(\text{cod})\text{M}(\mu_3\text{-S})_2\text{Rh}_2(\text{CO})_2(\text{PPh}_3)_2]$ ($\text{M} = \text{Pd}$, **8**; Pt , **9**), $[(\text{PPh}_3)_2\text{Pt}(\mu_3\text{-S})_2\text{Rh}_2(\text{CO})_2(\text{PPh}_3)_2]$ (**10**) and $[(\eta^6\text{-C}_6\text{H}_6)\text{Ru}(\mu_3\text{-S})_2\text{Rh}_2(\text{CO})_2(\text{PPh}_3)_2]$ (**12**), with PdRh_2 , PtRh_2 and RuRh_2 trimetallic cores. The aggregates derived from $[\text{Rh}(\mu\text{-SH})(\text{CO})(\text{PPh}_3)_2]$ were isolated as a mixture of *trans* and *cis* isomers in which the *trans* isomer predominates. Reaction of $[\text{Rh}(\mu\text{-SH})\{\text{P}(\text{O}i\text{Pr})_3\}_2]$ with 2 equiv. of *n*-BuLi at 253 K followed by addition of $[\text{Cp}^*\text{IrCl}_2]$ gave $[\text{Cp}^*\text{Ir}(\mu_3\text{-S})_2\text{Rh}_2\{\text{P}(\text{O}i\text{Pr})_3\}_4]$ (**4**) and $[\text{Cp}^*\text{Ir}(\mu_3\text{-S})_2\text{Rh}_2\{\text{P}(\text{O}i\text{Pr})_3\}_4]$ (**5**) in 3:2 ratio. The RuRh_2 compound $[(\eta^6\text{-C}_6\text{H}_6)\text{Ru}(\mu_3\text{-S})_2\text{Rh}_2\{\text{P}(\text{O}i\text{Pr})_3\}_4]$ (**11**) was prepared similarly from $[\text{Rh}(\mu\text{-SH})\{\text{P}(\text{O}i\text{Pr})_3\}_2]$ and $[(\eta^6\text{-C}_6\text{H}_6)\text{RuCl}_2]$ using *n*-BuLi as deprotonating agent. The molecular structures of compounds **3**, **6**, **7**, **9** and **11** have been determined by X-ray analysis. The trinuclear complexes exhibit an asymmetric triangular metal core with two triply bridging sulfido ligands resulting in a distorted trigonal-bipyramidal $\text{M}_3(\mu_3\text{-S})_2$ heterometallic metal-sulfur core.

Introduction

The chemistry of transition metal sulfido clusters has been attracting significant attention because of their relation to the active sites of certain metalloenzymes and industrial metal sulfide catalysts for hydrotreating processes.¹ The development of rational synthetic methods has allowed for the preparation of a wide range of multimetallic cores with bridging sulfido ligands having the desired metal composition and metal-sulfur framework.^{2,3} In this context, hydrosulfido metal complexes are fundamental building blocks for the rational synthesis of sulfido-bridged homo- and heterometallic clusters.⁴ Mononuclear bis(hydrosulfido) complexes, $\text{M}(\text{SH})_2$, or dinuclear compounds bridged by two hydrosulfido ligands, $\text{M}(\mu\text{-SH})_2\text{M}$, have turned out to be useful precursors for sulfido-bridged clusters.⁵

The complexes $[\text{Cp}_2\text{M}(\text{SH})_2]$ ($\text{M} = \text{Mo}, \text{W}$),⁶ $[\text{Cp}^*\text{M}(\text{SH})_2(\text{PR}_3)]$ ($\text{M} = \text{Rh}, \text{Ir}$),⁷ $[\text{M}(\text{SH})_2(\text{diphos})]$ ($\text{M} = \text{Pd}, \text{Pt}$)⁸ or $[\text{Mo}(\text{SH})_2(\kappa^4\text{-P4})]$ ($\text{P4} = \text{meso-}o\text{-C}_6\text{H}_4(\text{PPhCH}_2\text{CH}_2\text{PPh}_2)_2$)⁹ have been investigated as metalloligands for the synthesis of both hydrosulfido- and sulfido-bridged compounds. Interestingly, the compounds $[\text{Cp}_2\text{Ti}(\text{SH})_2]$ and $[\text{Cp}^{\text{tt}}_2\text{Zr}(\text{SH})_2]$ ($\text{Cp}^{\text{tt}} = \eta^5\text{-1,3-di-}tert\text{-butylcyclopentadienyl}$) have been successfully applied to the synthesis of *early-late* heterobimetallic complexes (ELHB) through additive deprotonation reactions with mono- and dinuclear d^8 rhodium and iridium compounds.¹⁰ This strategy has led to the preparation of heterotrinuclear, $[\text{TiM}_2]$ and $[\text{ZrM}_2]$,¹¹ and heterotetranuclear $[\text{TiM}_3]$ ($\text{M} = \text{Rh}, \text{Ir}$)¹² $d^0\text{-}d^8$ sulfido-bridged clusters and aggregates. On the other hand, the dinuclear compounds $[(\text{Cp}^*\text{MCl})_2(\mu\text{-SH})_2]$ ($\text{M} = \text{Ru}, \text{Rh}, \text{Ir}$) and $[(\text{Ru}(\eta^6\text{-$

arene) $\text{Cl}]_2(\mu\text{-SH})_2]$, have revealed as versatile precursors for the synthesis of sulfido clusters with nuclearities ranging from 3 to 10 by reaction with many transition metal and main-group metal species.¹³

We have described the preparation of bis(hydrosulfido)-bridged dinuclear rhodium(I) $[\text{Rh}(\mu\text{-SH})\text{L}_2]_2$ ($\text{L}_2 = (\text{CO})(\text{PR}_3)$, $\{\text{P}(\text{O}i\text{Pr})_3\}_2$) complexes using $\text{H}_2\text{S}(\text{g})$ as hydrosulfido ligand source.¹⁴ The complexes $[\text{Rh}(\mu\text{-SH})(\text{CO})(\text{PR}_3)_2]$ spontaneously transform in solution into the trinuclear hydrido-sulfido clusters $[\text{Rh}_3(\mu\text{-H})(\mu_3\text{-S})_2(\text{CO})_3(\text{PR}_3)_3]$ ($\text{R} = \text{Cy}, \text{Ph}$) with the release of $\text{H}_2\text{S}(\text{g})$ in a reversible way. However, the dinuclear complexes $[\text{Rh}(\mu\text{-SH})\text{L}_2]_2$ also behave as precursors for the controlled synthesis of diverse homo- and heterotrinuclear hydrido-sulfido clusters with the core $[\text{MRh}_2(\mu\text{-H})(\mu_3\text{-S})_2]$ ($\text{M} = \text{Rh}, \text{Ir}$).¹⁵ Interestingly, some of these clusters exhibited a mobile hydride ligand that migrates between edge-bridging sites through the bridging sulfido ligands.

Scheme 1. Synthetic strategies for the preparation of trinuclear sulfido-bridged clusters.

The formation of the hydrido-sulfido clusters is a consequence of the selective deprotonation of only one of the hydrosulfido ligands in the dinuclear complexes that in the presence of rhodium and iridium (I) metal fragments results in the formation of the $[\text{MRh}_2(\mu\text{-H})(\mu_3\text{-S})_2]$ core. However, the complexes $[\text{Rh}(\mu\text{-SH})\text{L}_2]_2$ could also be precursors of neutral trinuclear clusters with the core $[\text{MRh}_2(\mu_3\text{-S})_2]$ through the intermediate dianionic species $[\text{Rh}_2(\mu\text{-S})_2\text{L}_4]^{2-}$. In this context, related dinuclear precursors for the synthesis of sulfido-bridged aggregates are the anions $[\text{Cp}^*\text{Zr}(\mu\text{-S})_2\text{M}(\text{CO})_2]^-$ ($\text{M} = \text{Rh}, \text{Ir}$)¹⁶ or the metalloligand $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$.¹⁷ In the same way, the complexes $[(\text{Cp}^*\text{MCl})_2(\mu\text{-SH})_2]$ ($\text{M} = \text{Rh}, \text{Ir}$) can be considered as precursors for the Rh(III) and Ir(III) dinuclear platforms $[(\text{Cp}^*\text{M})_2(\mu\text{-S})_2]$ ($\text{M} = \text{Rh}, \text{Ir}$) by dehydrochlorination and, in fact, the synthesis of several homo- and heterometallic trinuclear $[\text{M}'\text{M}_2(\mu_3\text{-S})_2]$ and cubano-type $[\text{M}_2\text{M}'_2(\mu_3\text{-S})_4]$ clusters based on these platforms have been described.¹⁸

We report herein on the synthetic application of compounds $[\text{Rh}(\mu\text{-SH})\text{L}_2]_2$ ($\text{L}_2 = (\text{CO})(\text{PR}_3)$, $\{\text{P}(\text{O}^i\text{Pr})_3\}_2$) that constitute a versatile dinuclear Rh(I) platform for the controlled synthesis of mixed-metal sulfido-bridged aggregates with the core $[\text{MRh}_2(\mu_3\text{-S})_2]$ through the anionic $[\text{Rh}_2(\mu\text{-S})_2\text{L}_4]^{2-}$ species.

Results and discussion

Synthetic strategies for the preparation of trinuclear sulfido compounds

The monodeprotonation of bis-hydrosulfido dinuclear complexes $[\text{Rh}(\mu\text{-SH})\text{L}_2]_2$ ($\text{L}_2 = (\text{CO})(\text{PR}_3)$, $\{\text{P}(\text{O}^i\text{Pr})_3\}_2$) in the presence of cationic $d^8\text{-}[\text{M}(\text{diolate})]^+$ metal fragments has allowed for the preparation of trinuclear hydrido-sulfido clusters $[\text{L}_4\text{Rh}_2(\mu\text{-H})(\mu_3\text{-S})_2\text{M}(\text{diolate})]$ ($\text{M} = \text{Rh}, \text{Ir}$). The 48-valence-electron clusters can be described as composed by two metal-metal bonded 16-electron M^{II} metal atoms, with square-pyramidal geometries due to the coordination to the bridging hydride ligand, and a 16-electron square-planar M^{I} centre.^{14,15} The formation of the core $[\text{MRh}_2(\mu\text{-H})(\mu_3\text{-S})_2]$ is a consequence of the deprotonation of a

hydrosulfido ligand in the presence of d^8 metal fragments to give the trinuclear hydrosulfido-sulfido intermediates with the core $[\text{MRh}_2(\mu_3\text{-SH})(\mu_3\text{-S})]$ that collapse to the hydrido-sulfido clusters by a intramolecular proton transfer (pathway i, Scheme 1).

Alternatively, the deprotonation of both hydrosulfido ligands should result in the formation of the anionic $[\text{Rh}_2(\mu\text{-S})_2\text{L}_4]^{2-}$ species ($\text{L}_2 = (\text{CO})(\text{PR}_3)$, $\{\text{P}(\text{O}^i\text{Pr})_3\}_2$) that could be trapped by cationic ML_n^{2+} metal fragments to give neutral trinuclear aggregates with the core $[\text{MRh}_2(\mu_3\text{-S})_2]$ (pathway ii, Scheme 1). Thus, cations such as $d^6\text{-}[\text{Cp}^*\text{M}^{\text{III}}]^{2+}$ ($\text{M} = \text{Rh}, \text{Ir}$), $d^6\text{-}[(\eta^6\text{-C}_6\text{H}_6)\text{Ru}^{\text{II}}]^{2+}$, $d^8\text{-}[\text{M}^{\text{II}}(\text{cod})]^{2+}$ ($\text{M} = \text{Pd}, \text{Pt}$) and $d^8\text{-}[\text{Pt}^{\text{II}}(\text{PPh}_3)_2]^{2+}$, that are easily accessible from the corresponding choro complexes, are suitable metal fragments that fulfil the requirements for this synthetic strategy.

Synthesis and characterization of Rh_3 and IrRh_2 sulfido compounds

Reaction of $[\text{Rh}(\mu\text{-SH})(\text{CO})(\text{PPh}_3)]_2$ with 0.5 equiv of $[\text{Cp}^*\text{RhCl}_2]_2$ in CH_2Cl_2 in the presence of an excess of NEt_3 gave a black solution of $[\text{Cp}^*\text{Rh}(\mu_3\text{-S})_2\text{Rh}_2(\text{CO})_2(\text{PPh}_3)_2]$ (**1**). Compound **1** was isolated as black microcrystals in 86% yield after separation of the formed ammonium salt by extraction with toluene (Scheme 2). The formation of **1** was confirmed by the ESI-MS spectrum, which showed the molecular ion at m/z 1089. Compound **1** was isolated as mixture of *trans* and *cis* isomers, derived from the relative disposition of the PPh_3 and CO ligands, in which the *trans* isomer predominates. The *cis*-**1** isomer (C_s symmetry) was observed as a doublet centered at 37.04 ppm (d, $J_{\text{Rh-P}} = 166.5$ Hz) in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (C_6D_6 , 213K). However, the *trans*-**1** isomer (C_2 symmetry) showed a distinctive complex resonance corresponding to an $\text{AA}'\text{XX}'$ spin system due to a large $J_{\text{Rh-P}}$ coupling and smaller $^2J_{\text{Rh-P}}$, $^3J_{\text{P-P}}$ and $J_{\text{Rh-Rh}}$ coupling constants.¹⁹ The observed signal correlates well with the calculated spectrum using the parameters reported in the experimental section. The *trans*:*cis* ratio in purified **1** (62:38) is different from the ratio observed in the crude compound (50:50) and in the starting bis-hydrosulfido complex $[\text{Rh}(\mu\text{-SH})(\text{CO})(\text{PPh}_3)]_2$ (92:8). These data suggest that formation of **1** involves the opening of the dinuclear structure, in order to allow for isomerization, and that both isomers probably have different solubilities. The related heterometallic aggregate $[\text{Cp}^*\text{Ir}(\mu_3\text{-S})_2\text{Rh}_2(\text{CO})_2(\text{PPh}_3)_2]$ (**2**) was prepared from $[\text{Rh}(\mu\text{-SH})(\text{CO})(\text{PPh}_3)]_2$ and $[\text{Cp}^*\text{IrCl}_2]_2$ following the same synthetic protocol and isolated as a green microcrystalline solid in 68% yield as a mixture of the expected *trans* and *cis* isomers in 70:30 ratio (Scheme 2).

The deprotonation of $[\text{Rh}(\mu\text{-SH})\{\text{P}(\text{O}^i\text{Pr})_3\}_2]_2$ can be also accomplished by the mild base NEt_3 in spite of having less acidic hydrosulfido ligands than $[\text{Rh}(\mu\text{-SH})(\text{CO})(\text{PPh}_3)]_2$.¹⁴ Thus, when $[\text{Rh}(\mu\text{-SH})\{\text{P}(\text{O}^i\text{Pr})_3\}_2]_2$ was reacted with 0.5 equiv of $[\text{Cp}^*\text{RhCl}_2]_2$ in CH_2Cl_2 in the presence of excess of NEt_3 , the homometallic compound $[\text{Cp}^*\text{Rh}(\mu_3\text{-S})_2\text{Rh}_2\{\text{P}(\text{O}^i\text{Pr})_3\}_4]$ (**3**) was formed. Compound **3** was isolated as dark purple microcrystals in 76% yield. The spectroscopic data were in agreement with the C_{2v} structure (Scheme 2) and, consequently, a single resonance for the equivalent $\text{P}(\text{O}^i\text{Pr})_3$ ligands was seen at 113.51 ppm ($J_{\text{Rh-P}} = 292$ Hz) in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum.

* Chromatographic purification

Scheme 2. Synthesis of Rh₃ and IrRh₂ sulfido-bridged compounds.

The reaction of [Rh(μ-SH){P(OPh)₃}₂]₂ with [Cp*IrCl₂]₂ using NEt₃ as base did not give the expected heterometallic aggregate [Cp*Ir(μ₃-S)₂Rh₂{P(OPh)₃}₄] (**4**). However, the double deprotonation of the bis-hydrosulfido complex by the stronger base *n*-BuLi gave a yellow solution of the anion [Rh(μ-S){P(OPh)₃}₂]₂²⁻. Further reaction with [Cp*IrCl₂]₂ (0.5 equiv) and gradual warming to room temperature gave a deep green solution from which **4** was isolated as a green solid in low yield after chromatography purification. The investigation of the crude of reaction by NMR also evidenced the formation of the RhIr₂ compound [Cp*IrRh₂(μ₃-S)₂Rh{P(OPh)₃}₂] (**5**) with a **4**:**5** ratio of 3:2. Compound **5** has been characterized in solution and the proposed structure is shown in Scheme 2. The RhIr₂ core of **5** was established by MALDI-MS that showed the ion [Cp*Ir₂(μ₃-S)₂Rh{P(OPh)₃}₂]⁺ at *m/z* 1441.6 resulting from the loss of the chlorido ligand. The ¹H NMR of **5** in C₆D₆ showed two resonances in the Cp* region at 1.85 and 1.58 ppm which points to an asymmetric structure resulting from the coordination of the chlorido ligand at one of the Rh-Ir edges would fulfill the symmetry requirements, it would result in a 18 e⁻ Rh(I) centre. Taking into account that the equivalent P(OPh)₃ ligands in **5** were observed at similar chemical shift and comparable *J*_{Rh-P} coupling constant that those of **4** (**4**, 117.24 ppm, *J*_{Rh-P} = 293 Hz; **5**, 121.54 ppm, *J*_{Rh-P} = 290 Hz), the more likely structure should have a Cp*IrCl fragment with a terminal chlorido ligand, although a weak interaction with the adjacent rhodium centre can not be excluded.

Figure 1. Molecular structure of [Cp*Rh(μ₃-S)₂Rh₂{P(OPh)₃}₄] (**3**). Only *ipso* carbons of the phenyl rings have been represented for clarity. Bond distances (Å) and angles (deg) in the metal core: Rh(1)-S(1) 2.2960(7), Rh(1)-S(2) 2.2932(7), Rh(1)-G 1.7862(13), Rh(1)···Rh(2) 2.9415(4), Rh(1)···Rh(3) 2.9505(4), Rh(2)-S(1) 2.3361(7), Rh(2)-S(2) 2.3415(8), Rh(3)-S(1) 2.3386(7), Rh(3)-S(2) 2.3576(8), Rh(2)···Rh(3) 3.1500(4); S(1)-Rh(1)-S(2) 84.57(3), S(1)-Rh(2)-S(2) 82.62(3), S(1)-Rh(3)-S(2) 82.22(3), Rh(1)-S(1)-Rh(2) 78.84(2), Rh(1)-S(2)-Rh(2) 78.78(2), Rh(1)-S(1)-Rh(3) 79.07(2), Rh(1)-S(2)-Rh(3) 78.74(2), Rh(2)-S(1)-Rh(3) 84.73(2), Rh(2)-S(2)-Rh(3) 84.19(2) (G represents the centroid of the pentamethyl-cyclopentadienyl ligand).

Related precedents for sulfido-bridged IrRh₂ and Rh₃ compounds are [Cp*(PMe₃)Ir(μ₃-S)₂Rh₂(cod)₂]₂,²⁰ which was prepared from the bis-hydrosulfido mononuclear complex [Cp*Ir(SH)₂(PMe₃)], and [Cp*Rh(μ₃-S)₂Rh₂(CO)₄] obtained by thermolysis of a triangular RhRe₂ cluster in the presence of H₂S (g).²¹

The molecular structure of **3** has been determined by X-ray analysis and it is shown in Figure 1. **3** features an almost isosceles Rh₃ triangle capped, at both sides, by two triply bridging sulfido ligands, with a mean distance between the sulfur atoms and the trimetallic plane of 1.5438(5) Å, resulting in a trigonal bipyramidal Rh₃S₂ core. The Rh-Rh distances in the trimetallic core suggest the existence of two weak Rh-Rh interactions, Rh(1)-Rh(2) and Rh(1)-Rh(3), with distances of 2.9415(4) and 2.9505(4) Å. The Rh(2)-Rh(3) distance is slightly longer, 3.1500(4) Å, probably due to the bulkiness of the phosphite ligands, and shorter than in the bis-hydrosulfido rhodium precursor (3.2484(5) Å).¹⁴ This intermetallic bond distances scheme compares well with that observed in the closely related compound [Cp*Ir(μ₃-S)₂{Rh(cod)}₂], where two weak Rh-Ir interactions were proposed (Ir-Rh 2.9269(6) and 2.8772(5) Å, Rh-Rh 3.095(1) Å),²⁰ although all distances in the later heterometallic case are significantly shorter reflecting a greater intermetallic interaction. If the metal-metal interactions in **3** are ignored, the 48-valence-electron aggregate is composed by two formally 16-electron square-planar Rh^I centres, Rh(2) and Rh(3), coordinated to two additional triphenylphosphite ligands and a 16-electron Rh^{III} centre, Rh(1), with a distorted trigonal planar geometry by additional coordination to a Cp* ligand. The Cp* is orthogonal to the metallic plane with an angle of 89.47(8)° between the planes defined by the C(1)-C(5) ring carbons and the

Rh₃ core.

If compared to the parent dinuclear complex [Rh(μ -SH){P(OPh)₃}₂]₂, **3** shows a closing of the hinge angle defined between the two square-planar Rh^I coordination planes, from a value of 133.18(3)° in the starting complex to a value of 126.59(2)° in **3**. In addition, the Rh-S-Rh angles in the precursor dinuclear moiety (Rh(2)-S(1)-Rh(3) 84.73(2) and Rh(2)-S(2)-Rh(3) 84.19(2)°) are larger than those involving the Rh(1) metal centre (average of 78.86(1)°).

The Rh-S bond distances involving the added metallic fragment, Rh(1), are identical but somewhat shorter (2.2932 and 2.2960(7) Å) than the rest (average of 2.3434(4) Å), most probably reflecting the different electronic density present at the two type of metals, Rh^I or Rh^{III}; this latter value also evidences a shortening of the Rh^I-S bond distance upon coordination of the RhCp* moiety from the value observed in the parent dinuclear complex 2.3605(6) Å. Major distortions of the Rh^I metal coordination planes arise both from the *cis* arrangement of the bridging ligands (S-Rh^I-S 84.57 and 82.62(3)°) and from the steric influence of the bulky triphenylphosphite ligands (P-Rh^I-P angles of 99.04 and 98.17(3)°). In spite of the minor asymmetries observed, the whole molecule maintains a reasonable C_{2v} symmetry.

Scheme 3. Synthesis of PdRh₂ and PtRh₂ sulfido-bridged compounds.

Synthesis and characterization of PdRh₂ and PtRh₂ sulfido compounds

The mixed-metal sulfido-bridged aggregates [(cod)Pd(μ_3 -S)₂Rh₂{P(OPh)₃}₄] (**6**) and [(cod)Pt(μ_3 -S)₂Rh₂{P(OPh)₃}₄] (**7**) were prepared by reacting [Rh(μ -SH){P(OPh)₃}₂]₂ with the appropriate [MCl₂(cod)] (M = Pd, Pt) compound and NEt₃ in CH₂Cl₂. The compounds were obtained as light brown and yellow solids in good yields, following the established work up to remove the formed ammonium salt. In the same way,

[(cod)Pd(μ_3 -S)₂Rh₂(CO)₂(PPh₃)₂] (**8**) and [(cod)Pt(μ_3 -S)₂Rh₂(CO)₂(PPh₃)₂] (**9**) were obtained from [Rh(μ -SH)(CO)(PPh₃)₂]₂ and [MCl₂(cod)] (M = Pd, Pt) following the same synthetic protocol using THF as solvent (Scheme 3). Both compounds crystallized out in the reaction media, and were purified by washing with MeOH. The complexes were fully characterized by ¹H and ³¹P{¹H} NMR spectroscopy and MS, that confirmed the composition of the metal core.

Figure 2. Molecular structures of [(cod)Pd(μ_3 -S)₂Rh₂{P(OPh)₃}₄] (**6**) (a) and [(cod)Pt(μ_3 -S)₂Rh₂{P(OPh)₃}₄] (**7**) (b). Only *ipso* carbons of the phenyl rings have been represented for clarity. Bond distances (Å) and angles (deg) in the metal core: compound **6**, Pd-S(1) 2.317(2), Pd-S(2) 2.3104(19), Pd...Rh(2) 3.0645(10), Pd...Rh(3) 3.0757(9), Rh(2)-S(1) 2.3708(18), Rh(2)-S(2) 2.3631(18), Rh(2)...Rh(3) 3.1505(11), Rh(3)-S(1) 2.3611(18), Rh(3)-S(2) 2.3669(17), S(1)-Pd-S(2) 82.28(6); S(1)-Rh(2)-S(2) 80.04(6), S(1)-Rh(3)-S(2) 80.16(6), Pd-S(1)-Rh(2) 81.65(6), Pd-S(1)-Rh(3) 82.22(6), Rh(2)-S(1)-Rh(3) 83.49(6), Pd-S(2)-Rh(2) 81.94(6), Pd-S(2)-Rh(3) 82.22(6), Rh(2)-S(2)-Rh(3) 83.53(6); compound **7**, Pt-S(1) 2.3141(12), Pt-S(2) 2.3217(11), Pt...Rh(2) 3.0829(7), Pt...Rh(3) 3.0906(8), Rh(2)-S(1) 2.3613(13), Rh(2)-S(2) 2.3630(13), Rh(2)...Rh(3) 3.0844(7), Rh(3)-S(1) 2.3652(13), Rh(3)-S(2) 2.3643(12), S(1)-Pt-S(2) 82.57(4); S(1)-Rh(2)-S(2) 80.70(4), S(1)-Rh(2)-P(2) 176.14(5), S(1)-Rh(3)-S(2) 80.59(4), M-S(1)-Rh(2) 82.50(4), Pt-S(1)-Rh(3) 82.66(4), Rh(2)-S(1)-Rh(3) 81.47(4), M-S(2)-Rh(2) 82.30(4), Pt-S(2)-Rh(3) 82.52(4), Rh(2)-S(2)-Rh(3) 81.45(4).

Compounds **8** and **9** were isolated as a mixture of the *trans* and *cis* isomers being the former the major isomer in both cases. It is

noteworthy that the *trans/cis* ratio in crude **9**, 56:44, was quite different from the 84:16 ratio observed in the isolated compound. This fact is a consequence of the different solubility because the interconversion between both isomers has not been observed. The *trans* isomers of **8** and **9** were easily identified in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum due to the characteristic AA'XX' spin systems which were observed at 38.17 and 38.99 ppm, respectively. In contrast, the *cis* isomers showed a doublet at 37.19 and 37.96 ppm, respectively, with standard $J_{\text{Rh-P}}$ coupling constants (160–170 Hz). In the same way, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **6** and **7** showed a doublet for the equivalent $\text{P}(\text{OPh})_3$ ligands at 113.32 and 114.58 ppm ($J_{\text{Rh-P}} = 285\text{--}290$ Hz), respectively, in agreement with their C_{2v} symmetry. On the other hand, the equivalent olefinic protons of the cod ligand in **6** and **7** were observed as a broad resonance in the ^1H NMR spectra. However, each isomer of **8** and **9** showed two resonances as was expected for the symmetry of the aggregates. Interestingly, both C=H resonances in the *cis* isomer were observed at very different chemical shifts (δ 5.58 and 4.74 ppm for **8**, C_s symmetry) compared to the *trans* isomer (δ 5.27 and 5.05 ppm for **8**, C_2 symmetry). In addition, the C=H resonances of the *trans* isomer of **9**, at δ 4.77 and 4.65 ppm, showed the platinum satellites with a $J_{\text{Pt-H}}$ of 50 Hz.

Figure 3. Molecular structure of $[(\text{cod})\text{Pt}(\mu_3\text{-S})_2\text{Rh}_2(\text{CO})_2(\text{PPh}_3)_2]$ (**9**). The labelling scheme reflects the imposed C_2 crystallographic symmetry (primed atoms refer to symmetry equivalents through symmetry transformation: $I-x, y, 1/2-z$). Bond distances (Å) and angles (deg) in the metal core: Pt-S(1) 2.3120(7), Pt...Rh(2) 3.0572(3), Rh(2)-S(1) 2.3594(7), Rh(2)-S(1') 2.3704(7), Rh(2)...Rh(2') 3.1135(4), S(1)-Pt-S(1') 83.18(3), S(1)-Rh(2)-S(1') 80.93(3), Pt-S(1)-Rh(2) 81.75(2), Pt-S(1)-Rh(2'), 81.52(2), Rh(2)-S(1)-Rh(2') 82.34(2).

The molecular structures of **6**, **7** and **9** have been determined by single crystal X-ray analysis and are shown in Figures 2 and 3. The three heterometallic aggregates consist of a triangular metal core composed of two $d^8\text{-Rh}^{\text{I}}$ atoms and a different $d^8\text{-M}^{\text{II}}$ ($\text{M} = \text{Pd}, \text{Pt}$) centre exhibiting square-planar coordinations. The central $\text{MRh}_2(\mu_3\text{-S})_2$ moiety results in a distorted trigonal bipyramid with the S atoms out of the trimetallic plane by 1.5221(12) in **6**, 1.5293(10) in **7** and 1.5347(6) Å in **9**, similar values to that observed in **3**, 1.5438(5) Å.

Compounds **6** and **7** show a further closing of the hinge angle defined between the two square-planar Rh^{I} coordination planes, from a value of $126.59(2)^\circ$ in **3**, to a value of $121.37(4)^\circ$ in **6** and $117.44(3)^\circ$ in **7** due to the higher steric requirement of the cod ligand if compared with that of the Cp^* . The presence of less sterically demanding terminal ligands in **9**, PPh_3 and CO, allows this angle to open till a value of $125.67(2)^\circ$.

It is noteworthy to comment that compounds **6** and **9** display a similar pattern of intermetallic distances to that described in **3**, with two shorter Rh...M distances and a longer Rh...Rh separation (3.0645(10) and 3.0757(9) vs. 3.1505(11) Å in **6**, and 3.0572(3) vs. 3.1135(4) Å in **9**). However, all the three intermetallic distances are nearly identical in **7** with values in a narrow range, 3.0829–3.0906(8) Å. In spite of the different terminal ligands bonded to the Rh^{I} atoms, neither the Rh-S bond distances, nor the M-S bond separations, display significant differences, with statistically identical mean values in all the three structures (2.3655(9) and 2.3137(14) in **6**, 2.3635(7) and 2.3179(8) in **7**, and 2.3649(5) and 2.3120(7) Å in **9**). The major difference observed in the bond distances concerns the coordination of the cod ligand to the two diverse metals, Pd (**6**) and Pt (**7** and **9**), showing shorter M-C separations (and longer C=C bond distances) for the platinum aggregate.

Scheme 4. Synthesis of RuRh_2 sulfido-bridged compounds.

Attempts to prepare PtRh_2 sulfido compounds containing the metal fragment $d^8\text{-[Pt(PPh}_3)_2]^{2+}$ starting from $[\text{Rh}(\mu\text{-SH)}\{\text{P}(\text{OPh})_3\}_2]_2$ were unsuccessful, even using $n\text{-BuLi}$ as deprotonating agent. However, the deprotonation of $[\text{Rh}(\mu\text{-SH})(\text{CO})(\text{PPh}_3)_2]_2$ with NEt_3 in the presence of *cis*- $[\text{PtCl}_2(\text{PPh}_3)_2]$ gave $[(\text{PPh}_3)_2\text{Pt}(\mu_3\text{-S})_2\text{Rh}_2(\text{CO})_2(\text{PPh}_3)_2]$ (**10**) that was isolated as a yellow solid in 63% yield (Scheme 3). In contrast with the precedent aggregates, the isomer having a *cis* disposition of the PPh_3 ligands in the Rh_2 dinuclear subunit predominates, and a *trans:cis* ratio of 32:68 was determined by $^{31}\text{P}\{^1\text{H}\}$ NMR where both isomers are easily identified through the resonances of the “ $\text{Pt}(\text{PPh}_3)_2$ ” metal fragment (see Supplementary information). It is worth noting that the IR spectrum of **10** in CH_2Cl_2 features two strong characteristic $\nu(\text{CO})$ bands at 1954 and 1942 cm^{-1} , as found in the aggregates derived from $[\text{Rh}(\mu\text{-SH})(\text{CO})(\text{PPh}_3)_2]_2$, which is in agreement with the symmetry of both isomers.

Synthesis and characterization of RuRh_2 sulfido compounds

The aggregate $[(\eta^6\text{-C}_6\text{H}_6)\text{Ru}(\mu_3\text{-S})_2\text{Rh}_2\{\text{P}(\text{O}i\text{Pr})_3\}_4]$ (**11**) was prepared by reacting $[(\eta^6\text{-C}_6\text{H}_6)\text{RuCl}_2]_2$ (1 equiv) with the dianion $[\text{Rh}_2(\mu\text{-S})_2\{\text{P}(\text{O}i\text{Pr})_3\}_4]^{2-}$, generated in situ by deprotonation of $[\text{Rh}(\mu\text{-SH})\{\text{P}(\text{O}i\text{Pr})_3\}_2]_2$ with a slight excess of *n*-BuLi in THF at 253 K. When the reaction was conducted with the stoichiometric amount of $[(\eta^6\text{-C}_6\text{H}_6)\text{RuCl}_2]_2$ (0.5 equiv) the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the crude compound revealed the presence of unreacted starting material. Compound **11** was isolated as a purple solid in 52 % yield (based on rhodium) after the separation of an insoluble material and the LiCl formed. In sharp contrast, $[(\eta^6\text{-C}_6\text{H}_6)\text{Ru}(\mu_3\text{-S})_2\text{Rh}_2(\text{CO})_2(\text{PPh}_3)_2]$ (**12**) was prepared from $[\text{Rh}(\mu\text{-SH})(\text{CO})(\text{PPh}_3)]_2$ and the stoichiometric amount of $[(\eta^6\text{-C}_6\text{H}_6)\text{RuCl}_2]_2$ (0.5 equiv), using NEt_3 as deprotonating agent, and obtained as a brown solid in 42% yield (Scheme 4).

Figure 4. Molecular structure of $[(\eta^6\text{-C}_6\text{H}_6)\text{Ru}(\mu_3\text{-S})_2\text{Rh}_2\{\text{P}(\text{O}i\text{Pr})_3\}_4]$ (**11**). Only *ipso* carbons of the phenyl rings have been represented for clarity. Bond distances (Å) and angles (deg) in the metal core: Ru-S(1) 2.3271(6), Ru-S(2) 2.3198(6), Ru-G 1.6751(11), Ru-Rh(2) 2.8996(3), Ru-Rh(3) 3.0007(4), Rh(2)-S(1) 2.3305(6), Rh(2)-S(2) 2.3439(6), Rh(3)-S(1) 2.3350(6), Rh(3)-S(2) 2.3425(6), Rh(2)-Rh(3) 3.1489(3); S(1)-Ru-S(2) 83.68(2), S(1)-Rh(2)-S(2) 83.07(2), S(1)-Rh(3)-S(2) 83.01(2), P(3)-Rh(3)-P(4) 90.60(2), Ru-S(1)-Rh(2) 77.004(19), Ru-S(1)-Rh(3) 80.13(2), Rh(2)-S(1)-Rh(3) 84.90(2), Ru-S(2)-Rh(2) 76.882(18), Ru-S(2)-Rh(3) 80.123(19), Rh(2)-S(2)-Rh(3) 84.43(2) (G represents the centroid of the arene ligand).

The composition of the metal core in both compounds was established by the MS-ESI that showed the corresponding molecular ions. In addition, the ESI+ spectrum of **12** showed dicationic species resulting from the loss of a sulfido ligand and carbonyl or arene/carbonyl ligands at *m/z* 486.9 and 447.9, respectively. The arene ligand in **11** was observed at 4.47 ppm in the ^1H NMR spectrum. Compound **12** showed two resonances at 5.38 and 5.36 ppm corresponding to the arene ligand of the *trans* and *cis* isomers (64:36 ratio), respectively.

The molecular structure of **11** has been determined by X-ray analysis and is shown in Figure 4. The whole molecule resembles quite well the molecular structure of **3** where the 'RhCp*' fragment has been substituted by an isoelectronic 'Ru($\eta^6\text{-C}_6\text{H}_6$)'

group. The molecule exhibits a $\text{Ru}(\mu_3\text{-S})_2\text{Rh}_2$ bipyramidal core, configured from two square-planar $d^8\text{-Rh}^{\text{I}}$ units and a distorted planar tricoordinated $d^6\text{-Ru}^{\text{II}}$ moiety. The molecular parameters are rather similar to those observed in **3**; thus the sulfur atoms are 1.5497(4) Å out of the plane defined by the three metal (1.5438(5) Å in **3**).

Although the intermetallic separations in the heterometallic triangle show a similar pattern to that observed in **3** (and also in **6** and **9**),- with two shorter Rh...M distances and a Rh-Rh longer one,- a difficult-to-explain asymmetry appears in this structure where the two shorter separations are significantly different, 2.8996(3) and 3.0007(4) Å, diverse also from the longer Rh-Rh distance, 3.1489(3) Å. This asymmetry also seems to affect the Rh-S bond distances which show statistically different values for both chemically identical Rh-S links: consider, for instance, 2.3305(6) for Rh(2)-S(1) and 2.3439(6) Å for Rh(2)-S(2). As in **3**, the ideal addition of the 'Ru($\eta^6\text{-C}_6\text{H}_6$)' fragment to the dinuclear parent compound $[\text{Rh}(\mu\text{-SH})\{\text{P}(\text{O}i\text{Pr})_3\}_2]_2$ originates a closing of the hinge angle defined by the two square-planar Rh^{I} coordination planes, from the starting value of $133.18(3)^\circ$,¹⁴ to a value of $127.57(1)^\circ$ in **11**.

Conclusions

The bis-hydrosulfido-bridged dinuclear rhodium(I) complexes $[\text{Rh}(\mu\text{-SH})(\text{CO})(\text{PR}_3)_2]$ and $[\text{Rh}(\mu\text{-SH})\{\text{P}(\text{O}i\text{Pr})_3\}_2]$ are useful synthetic precursors for a series of mixed-metal neutral sulfido-bridged aggregates with trigonal-bipyramidal cores $[\text{MRh}_2(\mu_3\text{-S})_2]$ (M = Rh, Ir, Pd, Pt and Ru). The synthesis of the compounds results from the deprotonation of both hydrosulfido ligands in combination with their reaction with the suitable dicationic metal fragments: $d^6\text{-}[\text{Cp}^*\text{M}^{\text{III}}]^{2+}$ (M = Rh, Ir), $d^8\text{-}[\text{M}^{\text{II}}(\text{cod})]^{2+}$ (M = Pd, Pt), $d^8\text{-}[\text{Pt}^{\text{II}}(\text{PPh}_3)_2]^{2+}$ and $d^6\text{-}[(\eta^6\text{-C}_6\text{H}_6)\text{Ru}^{\text{II}}]^{2+}$, available from the corresponding chloro complexes. The formation of the metal core likely involves the formation hydrosulfido-bridged heteropolynuclear intermediates that undergo dehydrochlorination in the presence of the mild base triethylamine. However, in the case of complex $[\text{Rh}(\mu\text{-SH})\{\text{P}(\text{O}i\text{Pr})_3\}_2]_2$, with less acidic hydrosulfido ligands than in $[\text{Rh}(\mu\text{-SH})(\text{CO})(\text{PR}_3)_2]$ and bulky auxiliary phosphite ligands, the formation of the trinuclear complexes requires, in some cases, the generation in situ of the dianion $[\text{Rh}_2(\mu\text{-S})_2\{\text{P}(\text{O}i\text{Pr})_3\}_2]^{2-}$ by reaction with *n*-BuLi. Unfortunately, this synthetic approach sometimes results in the formation of aggregates with the undesired metal composition and/or unidentified byproducts. From the structural point of view, the studied molecular structures have been useful to show the flexibility of the parent $[\text{Rh}_2(\mu\text{-S})_2\text{L}_4]^{2-}$ metalloligand, that modifies its hinge interplanar angle to accommodate the coordination of different metal fragments according with their electronic and steric requirements.

Experimental

General considerations

All manipulations were performed under a dry argon atmosphere using Schlenk-tube techniques. All reactions were carried out at room temperature (RT) unless otherwise stated. Solvents were obtained from a Solvent Purification System (Innovative Technologies). The compounds $[\text{Cp}^*\text{MCl}_2]_2$ (M = Rh, Ir),²²

[MCl₂(cod)] (M = Pd, Pt),²³ [(η⁶-C₆H₆)RuCl₂]₂²⁴ and *cis*-[PtCl₂(PPh₃)₂]²⁵ were prepared according to literature procedures. [Rh(μ-SH){P(OPh)₃}₂]₂ and [Rh(μ-SH)(CO)(PPh₃)₂] were prepared following the synthetic procedure recently described.¹⁴ Triethylamine was obtained from Aldrich and used as received. ¹H and ³¹P{¹H} NMR spectra were recorded on a Bruker Avance 300 (300.13 and 121.50 MHz), Bruker Avance 400 MHz (400.13 and 161.99 MHz) and Bruker Avance 500 MHz (500.13 and 202.45 MHz) spectrometers. Chemical shifts are reported in parts per million and referenced to SiMe₄ using the signal of the deuterated solvent (¹H) and 85% H₃PO₄ (³¹P) as external reference, respectively. Assignments in complex NMR spectra were done by simulation with the program gNMR© v 3.6 (Cherwell Scientific Publishing Limited) for Macintosh. IR spectra were recorded on a Nicolet-IR 550 spectrometer. Elemental C, H and N analysis were performed in a Perkin-Elmer 2400 CHNS/O microanalyzer. We were unable to obtain satisfactory elemental analyses for the RuRh₂ compounds because of their air sensitivity although their identity and purity was established by NMR spectroscopy. Electrospray mass spectra (ESI-MS) were recorded on a Bruker MicroTof-Q using sodium formate as reference. MALDI-TOF mass spectra were obtained on a Bruker MICROFLEX spectrometer using DCTB (*trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile) or ditranol as matrix.

[Cp*Rh(μ₃-S)₂Rh₂(CO)₂(PPh₃)₂] (1)

NEt₃ (100 μL, 0.72 mmol) and [Cp*RhCl₂]₂ (0.022 g, 0.035 mmol) were successively added to a yellow solution of [Rh(μ-SH)(CO)(PPh₃)₂] (0.060 g, 0.070 mmol) in CH₂Cl₂ (5 mL) to give a black solution, which was stirred for 30 min. The solvent was removed under reduced pressure and the residue extracted with toluene (2 x 2 mL) and then filtered. The solution was evaporated under vacuum and the residue dissolved in CH₂Cl₂ (1 mL) and layered with *n*-hexane (8 mL) and kept at 243 K to give black microcrystals. The crystals were washed with pentane (2 x 3 mL) and dried under vacuum. Yield: 0.066 g (86%). Found: C, 52.75; H, 4.22; S, 5.76. Calc. for C₄₈H₄₅O₂P₂Rh₃S₂: C, 52.96; H, 4.17; S, 5.89. ¹H NMR (C₆D₆, RT): δ 7.97 (, *o*-H, Ph, *trans*-1), 7.74 (m, *o*-H, Ph, *cis*-1), 7.10 (m, Ph), 7.07-6.96 (m, Ph), 1.46 (s, Cp*, *cis*-1), 1.45 (s, Cp*, *trans*-1); *trans*:*cis* ratio, 62:38. ³¹P{¹H} NMR (C₆D₆, 213K) δ: 37.04 (d, *J*_{Rh-P} = 166.5 Hz) (*cis*-1), 36.84 (dm, AA'XX' spin system, *J*_{Rh-P} = 171.7 Hz, ²*J*_{Rh-P} ≈ -0.8 Hz, ³*J*_{P-P} ≈ 6.4 Hz, *J*_{Rh-Rh} ≈ 6.5 Hz) (*trans*-1). MS (ESI+, CH₃CN, m/z): 1089.0 ([M+H]⁺, 30%), 925.0 ([M+H]⁺ - Cp* - CO, 100%). IR (CH₂Cl₂, cm⁻¹): ν(CO), 1956 (s), 1942 (s).

[Cp*Ir(μ₃-S)₂Rh₂(CO)₂(PPh₃)₂] (2)

NEt₃ (200 μL, 2.80 mmol) and [Cp*IrCl₂]₂ (0.047 g, 0.059 mmol) were successively added to a solution of [Rh(μ-SH)(CO)(PPh₃)₂] (0.100 g, 0.117 mmol) in CH₂Cl₂ (5 mL) at 273 K to give a green solution, which was stirred for 2 h. Work up as describe above for **1** gave the compound as a green microcrystalline solid. Yield: 0.094 g (68 %). Found: C, 48.71; H, 3.96; S, 5.24. Calc. for C₄₈H₄₅IrO₂P₂Rh₂S₂: C, 48.94; H, 3.85; S, 5.44. ¹H NMR (C₆D₆, RT): δ 7.98 (m, *o*-H, Ph, *trans*-2), 7.73 (m, *o*-H, Ph, *cis*-2), 7.12 (m, Ph), 7.07-6.95 (m, Ph), 1.56 (s, Cp*, *cis*-2), 1.54 (s, Cp*, *trans*-2); *trans*:*cis* ratio, 70:30. ³¹P{¹H} NMR (C₆D₆, 213K): δ

39.06 (d, *J*_{Rh-P} = 167.7 Hz) (*cis*-2), 38.52 (dm, AA'XX' spin system, *J*_{Rh-P} = 171.7 Hz, ²*J*_{Rh-P} ≈ -0.6 Hz, ³*J*_{P-P} ≈ 5.7 Hz, *J*_{Rh-Rh} ≈ 6.7 Hz) (*trans*-2). MS (ESI+, CH₃CN, m/z): 1178.9 ([M+H]⁺, 100 %). IR (CH₂Cl₂, cm⁻¹): ν(CO), 1959 (s), 1945 (s).

[Cp*Rh(μ₃-S)₂Rh₂{P(OPh)₃}₄] (3)

NEt₃ (150 μL, 1.08 mmol) was added to a yellow solution of [Rh(μ-SH){P(OPh)₃}₂]₂ (0.080 g, 0.053 mmol) in CH₂Cl₂ (5 mL). The solution was stirred for 10 min and then reacted with [Cp*RhCl₂]₂ (0.016 g, 0.026 mmol) to give a deep purple solution, which was stirred for 2.5 h. Work up as described above for **1** gave the compound as dark purple microcrystals. Yield: 0.070 g (76%). Found: C, 56.12; H, 4.18; S, 3.81. Calc. for C₈₂H₇₅O₁₂P₄Rh₃S₂: C, 56.30; H, 4.32; S, 3.67. ¹H NMR (C₆D₆, RT): δ 7.41 (d, 24H, *J*_{H-H} = 5.7 Hz, OPh), 6.99 (t, 24H, *J*_{H-H} = 5.7 Hz, OPh), 6.80 (t, 12H, *J*_{H-H} = 5.4 Hz, OPh), 1.42 (s, 15H, Cp*). ³¹P{¹H} NMR (C₆D₆, RT): δ 113.51 (d, *J*_{Rh-P} = 291.6 Hz). MS (ESI+, CH₃CN, m/z): 1749.1 ([M + H]⁺, 30%).

[Cp*Ir(μ₃-S)₂Rh₂{P(OPh)₃}₄] (4)

n-BuLi (0.16 mL, 1.53 M, 0.245 mmol) was added to a solution of [Rh(μ-SH){P(OPh)₃}₂]₂ (0.120 g, 0.079 mmol) in THF (5 mL) at 253 K to give an yellow solution in 15 min. [(Cp*IrCl)₂(μ-Cl)₂] (0.032 g, 0.040 mmol) was added and the temperature steadily increased to RT to give a deep green solution. The solution was stirred for 20 min, concentrated under reduced pressure, and the residue washed with MeOH and dried under vacuum. The crude product, that is a mixture of **4** and **5**, was dissolved in CH₂Cl₂ and then absorbed onto silica and transferred to a silica gel column (20 x 1.5 cm) slurry-packed with *n*-hexane. Elution with CH₂Cl₂/*n*-hexane (3:2) mixture gave a green solution, from which the compound was obtained as green microcrystals by crystallization with MeOH. Yield: 0.026 g (17%). Found: C, 52.07; H, 4.29; S, 3.92. Calc. for C₈₂H₇₅O₁₂P₄Rh₂IrS₂·CH₂Cl₂: C, 51.83; H, 4.03; S, 3.33. ¹H NMR (C₆D₆, RT): δ 7.41 (d, 24H, *J*_{H-H} = 7.8 Hz, OPh), 6.99 (t, 24H, *J*_{H-H} = 8.1 Hz, OPh), 6.77 (t, 24H, *J*_{H-H} = 7.2 Hz, OPh), 1.49 (s, 15H, Cp*). ³¹P{¹H} NMR (C₆D₆, RT): δ 117.24 (d, *J*_{Rh-P} = 293.4 Hz). MS (MALDI+, C₆D₆, DCTB, m/z): 1838.1 (M⁺, 5%), 1218.1 (M⁺ - 2 P(OPh)₃, 18%), 907.9 ([M + H]⁺ - 3 P(OPh)₃, 5%), 814.0 ([M + H]⁺ - 3 P(OPh)₃ - OPh, 100%).

[Cp₂*ClIr₂(μ₃-S)₂Rh{P(OPh)₃}₂] (5)

NMR and MS data: ¹H NMR (C₆D₆, RT): δ 7.51 (d, *J*_{H-H} = 6.0 Hz, 12H, OPh), 7.05 (t, *J*_{H-H} = 6.0 Hz, 12H, OPh), 6.85 (t, *J*_{H-H} = 5.4 Hz, 6H, OPh), 1.85 (s, 15H, Cp*), 1.58 (s, 15H, Cp*). ³¹P{¹H} NMR (C₆D₆, RT): δ 121.54 (d, *J*_{Rh-P} = 290.0 Hz). MS (MALDI+, C₆D₆, DCTB, m/z): 1441.6 (M⁺ - Cl, 10%), 1133.4 (M⁺ - Cl - P(OPh)₃, 10%), 914.0 (M⁺ - Cl - P(OPh)₃ - S - 2OPh, 100%).

[(cod)Pd(μ₃-S)₂Rh₂{P(OPh)₃}₄] (6)

NEt₃ (100 μL, 0.719 mmol) was added to a yellow solution of [Rh(μ-SH){P(OPh)₃}₂]₂ (0.050 g, 0.033 mmol) in CH₂Cl₂ (5 mL). The solution was stirred for 10 min and then reacted with [PdCl₂(cod)] (0.010 g, 0.035 mmol) to give a brown solution, which was stirred for 2 h. The solvent was removed under reduced pressure and the residue extracted with toluene (2 x 2 mL) and then filtered. The solution was concentrated under vacuum to ca. 1 mL and then *n*-hexane (10 mL) was added to give a light brown solid. The solid was collected by filtration,

washed with *n*-hexane and then vacuum-dried. Yield: 0.030 g (53%). Found: C, 55.44; H, 4.18; S, 3.49. Calc. for $C_{80}H_{72}O_{12}P_4PdRh_2S_2$: C, 55.68; H, 4.20; S, 3.72. 1H NMR (C_6D_6 , RT): δ 7.48 (d, 24H, $J_{H-H} = 5.7$ Hz, OPh), 6.98 (t, 24H, $J_{H-H} = 4.5$ Hz, OPh), 6.78 (t, 12H, $J_{H-H} = 5.6$ Hz, OPh), 4.67 (br, 4H, =CH, cod), 1.73 (br, 8H, >CH₂, cod). $^{31}P\{^1H\}$ NMR (C_6D_6 , RT): δ 113.32 (d, $J_{Rh-P} = 285.4$ Hz). MS (MALDI⁺, CH₂Cl₂, DIT, m/z): 1104.2 ($M^+ - 2 P(OPh)_3$, 10%), 996.1 ($M^+ - 2 P(OPh)_3 - cod$, 100%), 686.0 ($M^+ - 3 P(OPh)_3 - cod$, 20%).

10 **[(cod)Pt(μ_3 -S)₂Rh₂{P(OPh)₃]₄] (7)**

NEt₃ (100 μ L, 0.719 mmol) was added to a yellow solution of [Rh(μ -SH){P(OPh)₃]₂] (0.050 g, 0.033 mmol) in CH₂Cl₂ (5 mL). The solution was stirred for 10 min and then reacted with [PtCl₂(cod)] (0.013 g, 0.034 mmol) to give a yellow solution, 15 which was stirred for 2 h. Work up as describe above for **6** gave the compound as a golden yellow solid. Yield: 0.036 g (60%). Found: C, 53.01; H, 4.32; S, 3.43. Calc. for $C_{80}H_{72}O_{12}P_4PtRh_2S_2$: C, 52.96; H, 4.00; S, 3.53. 1H NMR (C_6D_6 , RT): δ 7.45 (d, 24H, $J_{H-H} = 5.7$ Hz, OPh), 6.97 (t, 24H, $J_{H-H} = 5.7$ Hz, OPh), 6.77 (t, 12H, $J_{H-H} = 5.4$ Hz, OPh), 4.21 (br, 4H, =CH, cod), 1.70 (br, 8H, >CH₂, cod). $^{31}P\{^1H\}$ NMR (C_6D_6 , RT): δ 114.58 (d, $J_{Rh-P} = 289.6$ Hz). MS (MALDI⁺, CH₂Cl₂, DCTB, m/z): 1814.1 (M^+ , 5%), 1503.2 ($M^+ - P(OPh)_3$, 5%), 1393.3 ($M^+ - P(OPh)_3 - C_8H_{12}$, 100%), 1193.1 ($M^+ - 2 P(OPh)_3$, 70%).

25 **[(cod)Pd(μ_3 -S)₂Rh₂(CO)₂(PPh₃)₂] (8)**

NEt₃ (160 μ L, 1.15 mmol) and [PdCl₂(cod)] (0.017 g, 0.060 mmol) were successively added to a solution of [Rh(μ -SH)(CO)(PPh₃)₂] (0.050 g, 0.058 mmol) in THF (5 mL). The solution was stirred for 30 min to give a light brown suspension 30 that was concentrated under reduced pressure (1-2 mL) and then filtered. The obtained light brown solid was washed with MeOH (3 x 2 mL) and dried under vacuum. Yield: 0.026 g (42 %). Found: C, 51.96; H, 4.08; S, 5.88. Calc. for $C_{46}H_{42}O_2P_2PdRh_2S_2$: C, 51.87; H, 3.97; S, 6.02. 1H NMR (C_6D_6 , RT): δ 8.06 (m, *trans*-**8**, *o*-H, Ph), 7.86 (m, *cis*-**8**, *o*-H, Ph), 7.13–7.10 (m, Ph), 7.05–7.01 (m, Ph), 7.00–6.95 (m, Ph), 5.58 (m, =CH, cod, *cis*-**8**), 5.27 (m, =CH, cod, *trans*-**8**), 5.05 (m, =CH, cod, *trans*-**8**), 4.74 (m, =CH, cod, *cis*-**8**) (=CH, cod), 2.10–1.93 (m, >CH₂, cod), 1.78–1.73 (m, >CH₂, cod), 1.63–1.56 (m, CH₂, cod); *trans*:*cis* ratio, 40 92:8. $^{31}P\{^1H\}$ NMR (C_6D_6 , RT): δ 38.17 (dm, AA'XX' spin system, $J_{Rh-P} = 165.9$ Hz, $^2J_{Rh-P} \approx -0.8$ Hz, $^3J_{P-P} \approx 5.2$ Hz, $J_{Rh-Rh} \approx 8.3$ Hz) (*trans*-**8**), 37.19 (d, $J_{Rh-P} = 163.0$ Hz) (*cis*-**8**). MS (MALDI⁺, CH₂Cl₂, DCTB, m/z): 1064.1 (M^+ , 30%), 1010.1 ($M^+ - 2 CO$, 85%), 899.9 ($M^+ - 2 CO - cod$, 100%). IR (CH₂Cl₂, cm⁻¹): $\nu(CO)$, 1958 (m), 1946 (s).

[(cod)Pt(μ_3 -S)₂Rh₂(CO)₂(PPh₃)₂] (9)

NEt₃ (160 μ L, 1.15 mmol) and [PtCl₂(cod)] (0.022 g, 0.058 mmol) were successively added to a yellow solution of [Rh(μ -SH)(CO)(PPh₃)₂] (0.050 g, 0.058 mmol) in THF (5 mL). The solution was stirred for 30 min to give a yellow suspension. The solvent was removed under reduced pressure and the residue washed with MeOH (3 x 2 mL) to give a pale yellow solid that was dried under vacuum. Yield: 0.053 g (78 %). Found: C, 48.06; H, 3.86; S, 5.39. Calc. for $C_{46}H_{42}O_2P_2PtRh_2S_2$: C, 47.88; H, 3.67; 55 S, 5.56. 1H NMR (C_6D_6 , RT): δ 8.04 (m, *o*-H, Ph, *trans*-**9**), 7.83

(m, *o*-H, Ph, *cis*-**9**), 7.15–7.09 (m, Ph), 7.04–7.02 (m, Ph), 6.99–6.92 (m, Ph), 5.13 (m, =CH cod, *cis*-**9**), 4.77 (m, $J_{Pt-H} \approx 50$ Hz, =CH cod, *trans*-**9**), 4.65 (m, $J_{Pt-H} \approx 50$ Hz, =CH cod, *trans*-**9**), 4.29 (m, =CH cod, *cis*-**9**), 1.95 (m, >CH₂, cod), 1.79 (m, >CH₂, cod), 1.60 (m, >CH₂, cod), 1.43 (m, >CH₂, cod). $^{31}P\{^1H\}$ NMR (C_6D_6 , RT): δ 38.99 (dm, AA'XX' spin system, $J_{Rh-P} = 167.2$ Hz, $^2J_{Rh-P} \approx 0.4$ Hz, $^3J_{P-P} \approx 5.4$ Hz, $J_{Rh-Rh} \approx 14.5$ Hz) (*trans*-**9**), 37.96 (d, $J_{Rh-P} = 165.9$ Hz) (*cis*-**9**); *trans*:*cis* ratio, 84:16. MS (MALDI⁺, CH₂Cl₂, DCTB, m/z): 1098.2 ($M^+ - 2 CO$, 20%), 1064.2 ($M^+ - 2 CO - S$, 100%). IR (CH₂Cl₂, cm⁻¹): $\nu(CO)$, 1964 (m), 1949 (s).

[(PPh₃)₂Pt(μ_3 -S)₂Rh₂(CO)₂(PPh₃)₂] (10)

NEt₃ (250 μ L, 1.80 mmol) was added to a yellow solution of [Rh(μ -SH)(CO)(PPh₃)₂] (0.080 g, 0.094 mmol) in CH₂Cl₂ (5 mL). The solution was stirred for 10 min and then reacted with *cis*-[PtCl₂(PPh₃)₂] (0.074 g, 0.094 mmol) to give a brown solution, which was stirred for 2.5 h. The solvent was removed under reduced pressure and the residue dissolved in toluene (2 x 2 mL) and then filtered. The solution was evaporated under vacuum and the residue washed with a CH₂Cl₂/MeOH mixture (1:8, 3 x 3 mL) 75 and MeOH to give the compound as a yellow solid. Yield: 0.093 g (63%). Found: C, 56.42; H, 3.90; S, 3.98. Calc. for $C_{74}H_{60}O_2P_4PtRh_2S_2$: C, 56.60; H, 3.85; S, 4.08. 1H NMR (C_6D_6 , RT): δ 7.99 (m, 6H), 7.93 (m, 6H), 7.77 (m, 12H), 7.65 (m, 6H), 7.29 (m, 6H), 7.07–6.71 (set of m, 30H). $^{31}P\{^1H\}$ NMR (C_6D_6 , RT): δ 36.66 (br dd, $J_{Rh-P} = 167.0$ Hz, $^4J_{P-P} = 8.4$ Hz) (*trans*-**10**), 32.73 (ddd, $J_{Rh-P} = 161.7$ Hz, $^4J_{P-P} = 12.8$ Hz, $^4J_{P-P} = 5.3$ Hz) (*cis*-**10**), 19.33 (dt, $^2J_{P-P} = 13.1$ Hz, $^4J_{P-P} = 5.3$ Hz, $J_{Pt-P} = 3293$ Hz) (*cis*-**10**), 17.13 (d, $^4J_{P-P} = 8.4$ Hz, $J_{Pt-P} = 3185$ Hz) (*trans*-**10**), 85 14.43 (dt, $^2J_{P-P} = 13.1$ Hz, $^4J_{P-P} = 12.8$ Hz, $J_{Pt-P} = 3182$ Hz) (*cis*-**10**); *trans*:*cis* ratio, 32:68. MS (MALDI⁺, CH₂Cl₂, DCTB, m/z): 1570.2 (M^+ , 5%), 1514.1 ($M^+ - 2 CO$, 100%). IR (CH₂Cl₂, cm⁻¹): $\nu(CO)$, 1954 (s), 1942 (s).

[(η^6 -C₆H₆)Ru(μ_3 -S)₂Rh₂{P(OPh)₃]₄] (11)

To a solution of [Rh(μ -SH){P(OPh)₃]₂] (0.060 g, 0.039 mmol) in THF (5 mL) at 253 K, *n*-BuLi (64 μ L, 1.6 M, 0.10 mmol) was added. The solution was stirred for 15 min and then reacted with [(η^6 -C₆H₆)RuCl₂]₂ (0.020 g, 0.040 mmol). The solution was allowed to warm to RT and stirred for 4 h to give a purple suspension. The solvent was removed under vacuum and the residue extracted with toluene (2 x 2 mL) and then filtered. The solution was brought to dryness under vacuum to give a dark purple solid. The solid was dissolved in CH₂Cl₂ (1 mL) and layered with MeOH (8 mL) and kept at 243 K to give black-purple microcrystals of the compound. The crystals were washed with MeOH (2 x 1 mL) and dried under vacuum. Yield: 0.035 g (52%). 1H NMR (C_6D_6 , RT): δ 7.40 (d, 24H, $J_{H-H} = 7.5$ Hz, OPh), 6.97 (t, 24H, $J_{H-H} = 7.5$ Hz, OPh), 6.78 (t, 12H, $J_{H-H} = 7.3$ Hz, OPh), 4.47 (s, 6H, C₆H₆). $^{31}P\{^1H\}$ NMR (C_6D_6 , RT): δ 115.15 (d, 105 $J_{Rh-P} = 288.4$ Hz). MS (ESI⁺, THF, m/z): 1691.0 ([M + H]⁺, 65%).

[(η^6 -C₆H₆)Ru(μ_3 -S)₂Rh₂(CO)₂(PPh₃)₂] (12)

NEt₃ (225 μ L, 1.62 mmol) and [(η^6 -C₆H₆)RuCl₂]₂ (0.022 g, 0.044 mmol) were successively added to a yellow solution of [Rh(μ -SH)(CO)(PPh₃)₂] (0.075 g, 0.088 mmol) in CH₂Cl₂ (5 mL). The

solution was stirred for 4 h to give a brown suspension. The solvent was removed under reduced pressure and the residue washed with MeOH (3 x 2 mL) and with a CH₂Cl₂/MeOH mixture (1:3, 2 mL) to give the compound as a brown solid. Yield: 0.038 g (42 %). ¹H NMR (CD₂Cl₂, RT): δ 7.63 (m, *trans*-**12**, *o*-H, Ph), 7.46 (m, *cis*-**12**, *o*-H, Ph), 7.40–7.33 (set of m, Ph), 7.23 (m, Ph), 5.38 (s, C₆H₆, *trans*-**12**), 5.36 (s, C₆H₆, *cis*-**12**); *trans*:*cis* ratio, 64:36. ³¹P{¹H} NMR (CD₂Cl₂, RT): δ 38.26 (br dm, AA'XX' spin system, *J*_{Rh-P} = 168.6 Hz) (*trans*-**12**), 36.00 (br d, *J*_{Rh-P} = 165.3 Hz) (*cis*-**12**). MS (ESI+, CH₂Cl₂, *m/z*): 1024.8 ([M – CO + Na]⁺, 27%), 952.8 ([M – C₆H₆ + H]⁺, 28%), 923.8 ([M – C₆H₆ – CO]⁺, 26%), 486.9 ([M – CO – S]²⁺, 100%), 447.9 ([M – C₆H₆ – CO – S]²⁺, 38%). IR (CH₂Cl₂, cm⁻¹): ν(CO), 1967 (s), 1951 (s).

15 Crystal Structure Determination

Single crystals for the X-ray diffraction study of **3** (red prisms) and **9** (golden yellow microcrystals) were grown by slow diffusion of diethyl ether into CH₂Cl₂ solutions of the complexes at 273 K. Suitable crystals of **6** (red needles), **7** (yellow blocks) and **11** (red prisms) were grown by slow diffusion of *n*-hexane into dichloromethane solutions of the compounds at 273 K. Data were collected on a Bruker SMART APEX CCD (**3**, **6**, and **7**) or in a Bruker APEX DUO (**11**) conventional area-detector diffractometers. In the case of **9**, data were collected in the single axis HUBER diffractometer of the BM16 CRG beamline at the ESRF. Data were measured in all cases at low temperature (100(2) K) and using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) for those crystals measured at local diffractometers or using Silicon(111) monochromated synchrotron radiation for **9** (λ = 0.73820 Å). Conventional data were processed using SAINT-PLUS²⁶ and corrected for absorption using a multiscan method applied with SADABS²⁷ program; synchrotron intensities were integrated with HKL2000 suite²⁸ and corrected for absorption through the use of SORTAV program.²⁹ The structures were solved by direct methods with SHELXS-86³⁰ and the refinement, by full-matrix least squares on *F*², was carried out with SHELXL-97³¹ with anisotropic displacement parameters for all non-disordered non-hydrogen atoms. Hydrogen atoms were included in calculated positions and refined with positional and displacement parameters in a riding model. Detected static disorder problems are described below.

Crystal Data for **3**: C₈₂H₇₅O₁₂P₄Rh₃S₂, *M*_r = 1749.15, monoclinic, space group *P*2₁/*n*, crystal size 0.14 x 0.08 x 0.07 mm, *a* = 18.570(2), *b* = 19.659(2), *c* = 21.045(2) Å, β = 106.824(2)°, *V* = 7354.1(14) Å³, *Z* = 4, ρ_{calc} = 1.580 g/cm³, μ(MoKα) = 0.873 mm⁻¹. Min. & max. trans. fact. 0.888 and 0.940, 78993 measured reflections (1.54 ≤ 2θ ≤ 28.34°), 17819 unique (*R*_{int} = 0.0564); number of data/restraints/parameters 17819/0/933; final *R*₁ = 0.0407 (*I* > 2σ(*I*)), *wR*₂ = 0.0772, *S* = 1.051 for all data; max difference peak/hole 0.912/-0.567 e/Å³.

Crystal Data for **6**: C₈₀H₇₂O₁₂P₄PdRh₂S₂, *M*_r = 1725.60, orthorhombic, space group *Pna*2₁, crystal size 0.22 x 0.07 x 0.05, *a* = 28.003(8), *b* = 11.553(3), *c* = 22.405(7) Å, *V* = 7248(4) Å³, *Z* = 4, ρ_{calc} = 1.581 g/cm³, μ(MoKα) = 0.905. Min. & max. trans. fact. 0.826 and 0.956, 80905 measured reflections (1.72 ≤ 2θ ≤ 26.73°), 15385 unique (*R*_{int} = 0.1186); number of data/restraints/parameters 15385/1/911; final *R*₁ = 0.0600 (*I* >

2σ(*I*)), *wR*₂ = 0.1002, *S* = 1.072 for all data; max. difference peak/hole 0.768/-1.092 e/Å³.

Crystal Data for **7**: C₈₀H₇₂O₁₂P₄PtRh₂S₂ · CH₂Cl₂, *M*_r = 1899.21, triclinic, space group *P*-1, crystal size 0.182 x 0.137 x 0.078, *a* = 13.019(3), *b* = 14.506(4), *c* = 23.261(6), α = 88.088(4), β = 79.405(4), γ = 63.931(4)°, *V* = 3873.1(16) Å³, *Z* = 2, ρ_{calc} = 1.629 g/cm³, μ(MoKα) = 2.489 mm⁻¹. Min. & max. trans. fact. 0.660 and 0.829, 48268 measured reflections (1.57 ≤ 2θ ≤ 28.48°), 18337 unique (*R*_{int} = 0.0552); number of data/restraints/parameters 18337/6/974; final *R*₁ = 0.0456 (*I* > 2σ(*I*)), *wR*₂ = 0.0922, *S* = 1.009 for all data; max. difference peak/hole 1.348/-0.937 e/Å³. Static disorder was observed for six independent phenyl rings of the phosphite ligands; they were modelled on the base of two moieties of equal occupancy. An additional disordered dichloromethane solvent molecule was observed in the crystal structure; two molecules, with complementary occupancies, were included in the last cycles of refinement.

Crystal Data for **9**: C₄₆H₄₂O₂P₂PtRh₂S₂ · CH₂Cl₂, *M*_r = 1238.74, monoclinic, space group *C*2/*c*, crystal size 0.078 x 0.0325 x 0.0195, *a* = 22.5720(10), *b* = 9.4620(5), *c* = 21.3660(10) Å, β = 103.623(5)°, *V* = 4434.9(4) Å³, *Z* = 4, ρ_{calc} = 1.855 g/cm³, μ(MoKα) = 0.73820 Å = 4.430 mm⁻¹. Min. & max. trans. fact. 0.892 and 1.391, 23463 measured reflections (2.73 ≤ 2θ ≤ 28.16°), 4729 unique (*R*_{int} = 0.0773); number of data/restraints/parameters 4729/0/276; final *R*₁ = 0.0332 (*I* > 2σ(*I*)), *wR*₂ = 0.0821, *S* = 1.073 for all data; max. difference peak/hole 1.400/-2.055 e/Å³.

Crystal Data for **11**: C₇₈H₆₆O₁₂P₄Rh₂RuS₂ · 0.5CH₂Cl₂, *M*_r = 1732.66, triclinic, space group *P*-1, crystal size 0.390 x 0.263 x 0.168, *a* = 14.1988 (9), *b* = 16.1145 (11), *c* = 17.0522 (11) Å, α = 89.6900 (10), β = 68.6920 (10), γ = 83.6650 (10)°, *V* = 3610.2 (4) Å³, *Z* = 2, ρ_{calc} = 1.594 g/cm³, μ(MoKα) = 0.905 mm⁻¹. Min. & max. trans. fact. 0.719 and 0.863, 39759 measured reflections (1.61 ≤ 2θ ≤ 29.58°), 18257 unique (*R*_{int} = 0.0183); number of data/restraints/parameters 18257/0/896; final *R*₁ = 0.0344 (*I* > 2σ(*I*)), *wR*₂ = 0.0940, *S* = 1.024 for all data; max. difference peak/hole 1.269/-1.056 e/Å³. Static disorder affecting one of the phenyl groups has been modeled with two complementary geometrically-restrained moieties.

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Notes and references

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Graphical abstract

Bis(hydrosulfido)-Bridged Dinuclear Rhodium(I) Complexes as a Platform for the Synthesis of Trinuclear Sulfido Aggregates with the Core $[MRh_2(\mu_3-S_2)]$ (M = Rh, Ir, Pd, Pt, Ru)

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Dinuclear rhodium(I) complexes, $[Rh(\mu-SH)(CO)(PPh_3)]_2$ and $[Rh(\mu-SH)\{P(OPh)_3\}_2]_2$, constitute versatile platforms for the controlled synthesis of trinuclear mixed-metal sulfido-bridged aggregates with trigonal-bipyramidal cores $[MRh_2\mu_3-S)_2]$ (M = Rh, Ir, Pd, Pt and Ru).