**On the Synthesis and Chemical Behaviour of the Elusive Bis(hydrosulfido)-
bridged Dinuclear Rhodium(I) Complexes $[\text{Rh}(\mu\text{-SH})(\text{CO})(\text{PR}_3)]_2$**

**Jesús J. Pérez-Torrente,* M. Victoria Jiménez, Marc A. F. Hernandez-Gruel, María J.
Fabra, Fernando J. Lahoz and Luis A. Oro* ^[a]**

[a] Dr. J. J. Pérez-Torrente, Dr. M. V. Jiménez, Dr. M. A. F. Hernandez-Gruel, M. J. Fabra, Dr. F. J. Lahoz,
Prof. Dr. L. A. Oro
Departamento de Química Inorgánica, Instituto Universitario de Catálisis Homogénea, Instituto de Ciencia
de Materiales de Aragón, Universidad de Zaragoza-C.S.I.C.
50009-Zaragoza (Spain).
Fax: (+34) 976761143
E-mail: oro@unizar.es, perez@unizar.es

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Abstract

Several bis(hydrosulfido)-bridged dinuclear rhodium(I) compounds, $[\text{Rh}(\mu\text{-SH})\text{L}_2]_2$, have been prepared from rhodium(I) acetylacetonato complexes, $[\text{Rh}(\text{acac})\text{L}_2]$, and $\text{H}_2\text{S}(\text{g})$. Reaction of $[\text{Rh}(\text{acac})\{\text{P}(\text{OPh})_3\}_2]$ with $\text{H}_2\text{S}(\text{g})$ affords the dinuclear bis(hydrosulfido)-bridged compound $[\text{Rh}(\mu\text{-SH})\{\text{P}(\text{OPh})_3\}_2]_2$ (**1**). However, reaction of complexes $[\text{Rh}(\text{acac})(\text{CO})(\text{PR}_3)]$ with $\text{H}_2\text{S}(\text{g})$ gives the dinuclear compound $[\text{Rh}(\mu\text{-SH})(\text{CO})(\text{PR}_3)]_2$ ($\text{R} = \text{Cy}$, **2**; $\text{R} = \text{Ph}$, **4**) and the trinuclear cluster $[\text{Rh}_3(\mu\text{-H})(\mu_3\text{-S})_2(\text{CO})_3(\text{PR}_3)_3]$ ($\text{R} = \text{Cy}$, **3**; $\text{R} = \text{Ph}$, **5**). The selective synthesis of both type of compounds has been carried out by control of the $\text{H}_2\text{S}(\text{g})$ concentration in the reaction media. The trinuclear hydrido-sulfido cluster $[\text{Rh}_3(\mu\text{-H})(\mu_3\text{-S})_2(\text{CO})_3(\text{PPh}_3)_3]$ (**5**) has been also obtained by reaction $[\text{Rh}(\mu\text{-SH})(\text{CO})(\text{PPh}_3)]_2$ (**4**) with $[\text{Rh}(\text{acac})(\text{CO})(\text{PPh}_3)]$ through the trinuclear hydrosulfido-sulfido intermediate $[\text{Rh}_3(\mu_3\text{-SH})(\mu_3\text{-S})(\text{CO})_3(\text{PPh}_3)_3]$. The molecular structure of complexes **1** and **3** has been determined by X-ray diffraction methods.

Compound **1** is stable in solution but complexes $[\text{Rh}(\mu\text{-SH})(\text{CO})(\text{PR}_3)]_2$ (**2** and **4**) slowly transform in solution into the trinuclear hydrido-sulfido clusters **3** and **5**, respectively, with the release of $\text{H}_2\text{S}(\text{g})$ in a reversible way. ^1H NMR kinetic experiments for the transformation of **4** into **5** have revealed that this transformation follows second-order type kinetic. The following activation parameters, $\Delta H^\ddagger = 24 \pm 3 \text{ kJmol}^{-1}$ and of $\Delta S^\ddagger = -223 \pm 8 \text{ JK}^{-1}\text{mol}^{-1}$, have been calculated from the determination of the second-order rate constants in the temperature range 30-45 °C. The large negative value of the activation entropy is consistent with an associative character of the rate-determining step. A plausible multistep mechanism based on the chemical behaviour of hydrosulfido metal complexes and compatible with the kinetic behaviour has been proposed.

Introduction

The synthesis, structure, reactivity and properties of transition metal hydrosulfido complexes has experienced an outstanding growth in recent years mainly owing to the relationships existing between the coordination chemistry of hydrosulfido metal complexes and bioinorganic chemistry, geochemistry and catalysis.^[1] Interest in hydrosulfido complexes arise from their relevance to metalloenzymes containing S-H functionalities in their active site,^[2] the involvement in important mineralogical and geochemical transformations,^[3] and their role in the catalytic hydrodesulfurization (HDS) of fossil fuels.^[4]

Hydrosulfido metal complexes are also suitable building blocks for the synthesis of hydrosulfido- and sulfido-bridged polynuclear complexes and clusters because of the residual electron-donor ability of the M-S-H functionality. In fact, the rational synthesis of transition metal sulfido clusters with the desired metal-sulfur composition can be accomplished by using this versatile synthetic methodology.^[5] We have reported the application of mononuclear bis(hydrosulfido) titanium and zirconium complexes, $[\text{Cp}_2\text{Ti}(\text{SH})_2]$ and $[\text{Cp}^{\text{t}}_2\text{Zr}(\text{SH})_2]$ ($\text{Cp}^{\text{t}} = \eta^5\text{-1,3-di-}i\text{-tert-butylcyclopentadienyl}$), for the synthesis of *early-late* heterobimetallic complexes (ELHB). The deprotonation of these complexes with mono- and dinuclear d^8 rhodium and iridium compounds containing basic ligands has led to the preparation of heterotrinnuclear, $[\text{TiM}_2]$ ^[6] and $[\text{ZrM}_2]$,^[7] and heterotetranuclear $[\text{TiM}_3]$ ($\text{M} = \text{Rh, Ir}$)^[8] d^0 - d^8 sulfido-bridged complexes with incomplete cubane structures, and some unexpected $[\text{Ti}_2\text{Rh}_4]$ oxosulfido titanium-rhodium clusters with incomplete doubly-fused cubane structure.^[9] In the same way, Hidai and co-workers have met success in the application of bis(hydrosulfido)-bridged dinuclear $\text{M}^{\text{(III)}}$ complexes $[(\text{Cp}^*\text{MCl})_2(\mu_2\text{-SH})_2]$ ($\text{M} = \text{Ru, Rh, Ir}$) for the synthesis of tri- and pentanuclear heterometallic clusters with the cores $\text{M}'\text{M}_2(\mu_3\text{-S})_2$ and $\text{M}'\text{M}_4(\mu_3\text{-S})_4$,^[10] and cubano-type homometallic clusters $\text{M}_4(\mu_3\text{-S})_4$ ^[11] through condensation processes involving HCl elimination.

In searching for new precursors for the controlled synthesis of mixed-metal sulfido clusters, we thought about the potential of bis(hydrosulfido)-bridged dinuclear rhodium and iridium (I) complexes $[M(\mu\text{-SH})L_2]_2$. We were very much surprised to discover that, to best of our knowledge, the only reported example was the complex $[\text{Rh}(\mu\text{-SH})(\text{dippe})]_2$ (dippe = 1,2-bis(di-isopropylphosphine)ethane), described and structurally characterized by Jones and co-workers in 2004.^[12] This fact is in sharp contrast with the large number of alkyl-, aryl- and functionalized bis(thiolato)-bridged dinuclear rhodium and iridium complexes with a diversity of auxiliary ligands such as $[M(\mu\text{-SR})L_2]_2$ (L_2 = diolefin, $(\text{CO})_2$, $(\text{CO})(\text{PR}_3)$, $(\text{PR}_3)_2$), and $[M(\mu\text{-SR})(\text{CO})(\mu\text{-diphos})]_2$ ($M = \text{Rh, Ir}$).^[13] Noteworthy, several low valent homo- and heterodinuclear bis(hydrosulfido)-bridged dinuclear transition metal complexes have been reported, as for example, $[\{M(\text{CO})_n\}_2(\mu\text{-SH})_2]$ ($M = \text{Mn, W}$, $n = 4$; $M = \text{Fe}$, $n = 3$).^[14] In addition, some rhodium homo- and heterodinuclear complexes as $[\{\text{RhHCl}(\text{PPh}_3)_2\}_2(\mu\text{-SH})_2]$,^[15] $[\{(\text{triphos})\text{RhH}\}_2(\mu\text{-SH})_2][\text{BPh}_4]_2$,^[16] $[(\text{dppe})M(\mu\text{-SH})_2\text{Rh}(\text{PPh}_3)_2]$ ($M = \text{Pd, Pt}$)^[17] and $[\text{Cp}_2\text{Mo}(\mu\text{-SH})_2\text{Rh}(\text{PPh}_3)_2]$ ^[18] have also been described. Interestingly, the bis(thiolato) complex $[\text{Cp}_2\text{Ti}(\mu\text{-SMe})_2\text{Mo}(\text{CO})_4]$ has been obtained by alkylation of $[\text{Cp}_2\text{Ti}(\mu\text{-SH})_2\text{Mo}(\text{CO})_4]$.^[19]

On the other hand, it is well known that the 48-electron hydrido-sulfido clusters $[\text{M}_3(\mu\text{-H})(\mu_3\text{-S})_2(\text{cod})_3]$ are a common outcome in the reactions of complexes $[M(\mu\text{-Cl})(\text{cod})]_2$ ($M = \text{Rh, Ir}$) with NaSH .^[20] Alternative synthetic routes to dinuclear $[M(\mu\text{-SH})(\text{cod})]_2$ complexes from $[M(\text{acac})(\text{cod})]$ or $[M(\mu\text{-OMe})(\text{cod})]_2$ ($M = \text{Rh, Ir}$) and $\text{H}_2\text{S}(\text{g})$ as hydrosulfido ligand source have also proven to be unsuccessful as the trinuclear hydrido-sulfido clusters were generally formed.^[21] We report herein on the synthesis and characterization of bis(hydrosulfido)-bridged rhodium(I) complexes, $[\text{Rh}(\mu\text{-SH})(\text{CO})(\text{PR}_3)]_2$, and their spontaneous transformation into trinuclear hydrido-sulfido clusters $[\text{Rh}_3(\mu\text{-H})(\mu_3\text{-S})_2(\text{CO})_3(\text{PR}_3)_3]$.

Results and Discussion

Reaction of $[\text{Rh}(\text{acac})\{\text{P}(\text{OPh})_3\}_2]$ with $\text{H}_2\text{S}(\text{g})$. The reaction of $[\text{Rh}(\text{acac})\{\text{P}(\text{OPh})_3\}_2]$ with $\text{H}_2\text{S}(\text{g})$ in diethyl ether at 273 K gave a pale-yellow suspension of the bis(hydrosulfido)-bridged dinuclear compound $[\text{Rh}(\mu\text{-SH})\{\text{P}(\text{OPh})_3\}_2]_2$ (**1**) which was isolated in excellent yield (Scheme 1). The compound has been fully characterized by elemental analysis, FAB mass spectra and NMR. In addition, the molecular structure of compound **1** has been determined by X-ray and shows a bent structure with the hydrosulfido ligands adopting a *syn-endo* conformation (Figure 1).

The spectroscopic data for **1** are in accordance with the C_{2v} structure found in the solid state. Thus, a singlet resonance at δ 0.47 ppm was observed for the equivalent hydrosulfido ligands in the ^1H NMR spectrum in C_6D_6 and a slightly broad doublet centered at δ 117.2 ppm ($J(\text{Rh},\text{P}) = 283$ Hz) for the equivalent triphenylphosphite ligands in the ^{31}P NMR, as a consequence of smaller $^2J(\text{Rh},\text{P})$ (≈ 3 Hz) and $^3J(\text{P},\text{P})$ (≈ 15 and 8 Hz) couplings.^[7c] The ^1H NMR spectrum in $[\text{D}_8]\text{-toluene}$ at 223 K evidenced the broadening of the SH resonance (δ 0.39 ppm) which is probably a consequence of the partial freezing of the expected *syn-endo/syn-exo* interconversion operating at RT.^[13c, 22] In addition, the intensity of the SH resonance diminished when CD_3OD was added to a solution of the compound in C_6D_6 (H/D exchange) which is indicative of the slightly acidic character of the hydrosulfido ligands in **1**.

Reaction of $[\text{Rh}(\text{acac})(\text{CO})(\text{PR}_3)]$ ($\text{R} = \text{Cy}, \text{Ph}$) with $\text{H}_2\text{S}(\text{g})$. The reaction of $[\text{Rh}(\text{acac})(\text{CO})(\text{PCy}_3)]$ with $\text{H}_2\text{S}(\text{g})$ in tetrahydrofuran allowed the isolation of an orange solid that actually is a mixture of complexes $[\text{Rh}(\mu\text{-SH})(\text{CO})(\text{PCy}_3)]_2$ (**2**) (55%) and $[\text{Rh}_3(\mu\text{-H})(\mu_3\text{-S})_2(\text{CO})_3(\text{PCy}_3)_3]$ (**3**) (45%). However, both complexes can be prepared independently by careful control of the reaction conditions, in particular, the solvent and the reaction time.

Thus, compound **2** crystallized out as an orange-red solid when a concentrated tetrahydrofuran solution of $[\text{Rh}(\text{acac})(\text{CO})(\text{PCy}_3)]$ was stirred under $\text{H}_2\text{S}(\text{g})$ for 24h at RT, and was isolated in moderate yield. However, compound **3** was prepared in dichloromethane under the same experimental conditions in one hour, an isolated as an orange-red microcrystalline solid in good yield (Scheme 1).

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **2** in CDCl_3 showed a doublet at δ 51.43 ppm ($J(\text{Rh},\text{P}) = 156$ Hz, $^3J(\text{P},\text{P}) < 12$ Hz) for the equivalent PCy_3 ligands, and the ^1H NMR spectrum a triplet at δ -0.58 ppm, that became a singlet in the $^1\text{H}\{^{31}\text{P}\}$ NMR ($^3J(\text{H},\text{P}) = 3.3$ Hz), for the equivalent hydrosulfido ligands. These data are in full agreement with the existence of a single *trans* isomer of C_2 symmetry having a *syn* conformation of the hydrosulfido ligands (Scheme 1).

The hydrido ligand in **3** was observed in the ^1H NMR spectrum (CDCl_3) as a characteristic triplet of triplets at δ -14.33 ppm which is consistent with a μ_2 -H ligand ($J(\text{Rh},\text{H}) = 31$ Hz, $^2J(\text{P},\text{H}) = 3.3$ Hz). The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum showed three well defined resonances, indicating the non-equivalence of the PCy_3 ligands in the structure, and has been simulated using the chemical shifts and coupling constant of Table 1. These spectroscopic data are only compatible with a structure having an unsymmetrical disposition of the PCy_3 ligands in the equilateral triangular Rh_3 core with the hydride ligand bridging one of the edges with a relative *trans* disposition of the PCy_3 ligands (Scheme 1). Full assignment of the resonances comes from the 2D ^1H - ^{31}P HMBC spectrum that showed cross peaks between the hydride resonance and the resonances at δ 48.88 and 44.57 ppm (P_A and P_B , Table 1). The relative *trans* disposition of P_A and P_C has been inferred by the slightly large $J(\text{P}_\text{A},\text{P}_\text{C})$ coupling constant.

The reaction of $[\text{Rh}(\text{acac})(\text{CO})(\text{PPh}_3)]$ with $\text{H}_2\text{S}(\text{g})$ in tetrahydrofuran at 195 K gave a yellow suspension of compound $[\text{Rh}(\mu\text{-SH})(\text{CO})(\text{PPh}_3)]_2$ (**4**) that was isolated in excellent yield

(Scheme 1). Compound **4** was obtained as a mixture of *trans* (**4a**) and *cis* (**4b**) isomers in which the *trans* isomer predominates (92:8). The $^{31}\text{P}\{^1\text{H}\}$ NMR of both isomers consists of a doublet ($J(\text{Rh},\text{P}) \approx 160$ Hz) in agreement with equivalent PPh_3 ligands and a *syn* disposition of both hydrosulfido ligands. The equivalent hydrosulfido ligands of **4a** (C_2 symmetry) were observed as complex resonance at δ - 0.15 ppm in the ^1H NMR spectrum (C_6D_6) by coupling to both rhodium and phosphorous atoms (Figure 2). In contrast, the non-equivalent hydrosulfido ligands in **4b** (C_s symmetry) were observed as two triplets at δ -1.38 and -1.39 ppm that became two singlets in the $^1\text{H}\{^{31}\text{P}\}$ NMR indicating that the observed multiplicity is due to coupling with the two equivalent phosphorous atoms ($^3J(\text{P},\text{H}) = 6.5$ Hz). Interestingly, both isomers interconvert in solution as was evidenced by the cross peak observed in the ^1H - ^1H NOESY spectrum in C_6D_6 .

The stirring of a dichloromethane solution of $[\text{Rh}(\text{acac})(\text{CO})(\text{PPh}_3)]$ under a H_2S (g)/Ar (g) (1:1) atmosphere at room temperature resulted in the formation of a red solution from which $[\text{Rh}_3(\mu\text{-H})(\mu_3\text{-S})_2(\text{CO})_3(\text{PPh}_3)_3]$ (**5**) was isolated as red-violet microcrystals in good yield (Scheme 1). The spectroscopic data for **5** closely resemble those of compound **3** and consequently should be isostructural. In particular, the bridging hydrido ligand was observed as a triplet of triplets at δ -13.90 ppm in the ^1H NMR spectrum (C_6D_6) and the complex $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum featured three distinct resonances for the PPh_3 ligands. The simulation of the complex $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at 253 K in $[\text{D}_8]$ -toluene (Figure 3) in combination with the ^1H - ^{31}P HMBC spectrum has allowed the full characterization of the complex (Table 1). Thus, the hydrido ligand bridges the rhodium atoms with the smaller ($J(\text{Rh},\text{P})$ coupling constant (P_A and P_B) and, as expected, the largest $J(\text{P},\text{P})$ were observed between the PPh_3 ligands exhibiting a relative *trans* disposition (P_A - P_B and P_C - P_A).

Molecular structure of [Rh(μ -SH){P(OPh)₃}₂]₂ (1**) and [Rh₃(μ -H)(μ_3 -S)₂(CO)₃(PCy₃)₃]₂ (**3**).**

Molecular drawings taking account of displacement ellipsoids are represented in figures 1 and 4; the most relevant bond distances and angles are collected in tables 2 and 3. Data concerning the crystallographic structural analysis are included in Table 4.

Complex **1** shows a dinuclear molecular structure having two identical ‘Rh{P(OPh)₃}₂’ moieties connected by a bent symmetrical bis(hydrosulfido) bridge. Both Rh^I metals exhibit distorted square-planar coordination environments with an interplanar angle of 133.18(3)°. A similar hinge angle has been observed (136.0°) in the 1,2-bis(di-isopropylphosphine)ethane analogue, [Rh(μ -SH)(dippe)]₂, where the preference of sulfur to pyramidalize and the presence of a weak metal-metal interaction (Rh-Rh 3.28 Å) have been suggested to rationalize the bent geometry.^[12] The Rh...Rh separation in **1**, 3.2484(5) Å, excludes any but the weakest intermetallic interaction. Major distortions of the metal coordination planes obviously arise from the *cis* disposition of the bridging ligands (mean bond angle 78.36(3)°). Although statistically significant, the minor differences observed in the Rh-P and Rh-S bond distances agree to consider an almost perfect C_{2v} symmetry. The quality of the structural analysis has allowed to identify a *syn-endo* conformation for the two bridging SH ligands.

The trinuclear complex **3** exhibits an asymmetric triangular metal core with two triply bridging sulfido ligands, at both sides of the Rh₃ plane, connecting three identical ‘Rh(CO)(PCy₃)’ moieties. An additional hydrido ligand bridges two metals (Rh(1)-Rh(3) 2.8418(11) Å) making this intermetallic distance the shortest and potentially indicative of the presence of a metal-metal bond; most likely, the steric interactions between the two bulky phosphines, in a relative *cis* disposition between Rh(2) and Rh(1), make this separation the longest (3.2681(11) Å). The third intermetallic separation, Rh(2)-Rh(3), is intermediate to the other ones (3.0900(11) Å). Each metal centre additionally coordinates a terminal carbonyl and

a tricyclohexylphosphine. As inferred from NMR data, the two phosphines bonded at Rh(1) and Rh(3) occupy relative *pseudo-trans* dispositions (P-Rh-Rh-P torsion angle 122.16(11)°), as well as those bonded to Rh(2) and Rh(3) (torsion 114.45(11)), while those linked to Rh(1) and Rh(2) exhibit a clear *pseudo-cis* relative situation (P(1)-Rh(1)-Rh(2)-P(2) 16.23(14)°).

All these structural parameters led us to interpret compound **3** as a 48 valence electrons cluster consisting of a metal-metal bonded Rh(μ -H)Rh unit with 16 electron configuration Rh^{II} centers having distorted square-pyramidal geometries, and a 16 electron square-planar Rh^I center. An alternative description with two Rh^I atoms with a metal-metal bond and a Rh^{III} center is unlikely on the light of the structural and spectroscopic data.

Formation of $[\text{Rh}_3(\mu\text{-H})(\mu_3\text{-S})_2(\text{CO})_3(\text{PR}_3)_3]$ versus $[\text{Rh}(\mu\text{-SH})(\text{CO})(\text{PR}_3)]_2$. The monitoring of the reaction of $[\text{Rh}(\text{acac})\{\text{P}(\text{OPh})_3\}_2]$ and $\text{H}_2\text{S}(\text{g})$ in C_6D_6 at RT showed the exclusive formation of $[\text{Rh}(\mu\text{-SH})\{\text{P}(\text{OPh})_3\}_2]_2$ (**1**) and Hacac in a fast and quantitative way. However, the reaction of $[\text{Rh}(\text{acac})(\text{CO})(\text{PCy}_3)]$ with $\text{H}_2\text{S}(\text{g})$ in CDCl_3 gave immediately a deep red solution of compounds *trans*- $[\{\text{Rh}(\mu\text{-SH})(\text{CO})(\text{PCy}_3)]_2$ (**2**) (27%) and $[\text{Rh}_3(\mu\text{-S})_2(\mu\text{-H})(\text{CO})_3(\text{PCy}_3)_3]$ (**3**) (73%), as was deduced from the ¹H NMR spectra. In the same way, the stirring of a solution of $[\text{Rh}(\text{acac})(\text{CO})(\text{PPh}_3)]$ in C_6D_6 under $\text{H}_2\text{S}(\text{g})$ gave a deep red-violet solution that contain $[\text{Rh}(\mu\text{-SH})(\text{CO})(\text{PPh}_3)]_2$ (**4**) (59%) and $[\text{Rh}_3(\mu\text{-H})(\mu_3\text{-S})_2(\text{CO})_3(\text{PPh}_3)_3]$ (**5**) (41%).

These results together with the key role played by the $\text{H}_2\text{S}(\text{g})$ concentration in the optimization of the reaction conditions for the synthesis of either $[\text{Rh}(\mu\text{-SH})(\text{CO})(\text{PR}_3)]_2$ or $[\text{Rh}_3(\mu\text{-H})(\mu_3\text{-S})_2(\text{CO})_3(\text{PR}_3)_3]$, strongly suggest that the formation of both types of complexes is a competitive process. Thus, when the concentration of $\text{H}_2\text{S}(\text{g})$ in the reaction media is high the protonation of $[\text{Rh}(\text{acac})(\text{CO})(\text{PR}_3)]$ by H_2S takes place preferably and results in the formation of the dinuclear compounds $[\text{Rh}(\mu\text{-SH})(\text{CO})(\text{PR}_3)]_2$. However, this process

competes with the deprotonation of the hydrosulfido ligands in $[\text{Rh}(\mu\text{-SH})(\text{CO})(\text{PR}_3)_2]$ by $[\text{Rh}(\text{acac})(\text{CO})(\text{PR}_3)]$ at low concentration of H_2S to give the trinuclear hydrosulfido-sulfido intermediates $[\text{Rh}_3(\mu_3\text{-SH})(\mu_3\text{-S})(\text{CO})_3(\text{PR}_3)_3]$ (not observed by NMR) that collapse to the hydrido-sulfido clusters $[\text{Rh}_3(\mu\text{-H})(\mu_3\text{-S})_2(\text{CO})_3(\text{PR}_3)_3]$ by a intramolecular proton transfer (Scheme 2). This reaction scheme also allows the rationalization of the experimental conditions used in the synthesis of both type of compounds. The synthesis of the hydrido-sulfido clusters was conducted in dichloromethane at room temperature whereas that the synthesis of $[\text{Rh}(\mu\text{-SH})(\text{CO})(\text{PR}_3)_2]$ requires tetrahydrofurane, and generally low temperature, because of the solubility of $\text{H}_2\text{S}(\text{g})$ is much higher in this solvent.

This proposal is strongly supported by several experimental observations. The compound $[\text{Rh}(\mu\text{-SH})(\text{CO})(\text{PPh}_3)_2]$ (**4**) reacted with $[\text{Rh}(\text{acac})(\text{CO})(\text{PPh}_3)]$ in C_6D_6 to give $[\text{Rh}_3(\mu\text{-H})(\mu_3\text{-S})_2(\text{CO})_3(\text{PPh}_3)_3]$ (**5**) and, actually, this is an alternative synthetic procedure for the synthesis of **5** also in good yield (70%). In contrast, $[\text{Rh}(\mu\text{-SH})\{\text{P}(\text{OPh})_3\}_2]$ (**1**) failed to react with $[\text{Rh}(\text{acac})\{\text{P}(\text{OPh})_3\}_2]$ in C_6D_6 which explains the high yield synthesis of **1** from $[\text{Rh}(\text{acac})\{\text{P}(\text{OPh})_3\}_2]$ and $\text{H}_2\text{S}(\text{g})$.

Conversion between $[\text{Rh}(\mu\text{-SH})(\text{CO})(\text{PR}_3)_2]$ and $[\text{Rh}_3(\mu\text{-H})(\mu_3\text{-S})_2(\text{CO})_3(\text{PR}_3)_3]$ complexes mediated by H_2S . The observed product distribution in the reaction of complex $[\text{Rh}(\text{acac})(\text{CO})(\text{PPh}_3)]$ with $\text{H}_2\text{S}(\text{g})$, and the high yield synthesis of the compound $[\text{Rh}(\mu\text{-SH})(\text{CO})(\text{PPh}_3)_2]$ (**4**) under the appropriate experimental conditions, strongly suggest that the interconversion between both type of complexes, **4** and **5**, could be operative (Scheme 3). Monitoring of a solution of **4** in C_6D_6 at room temperature showed evidence for the slow disappearance of **4** and the formation of the hydrido-sulfido cluster $[\text{Rh}_3(\mu\text{-H})(\mu_3\text{-S})_2(\text{CO})_3(\text{PPh}_3)_3]$ (**5**) along with H_2S that was observed as a singlet at δ 0.20 ppm in the ^1H NMR spectrum. This is a clean and rather slow transformation since a 70% of conversion was

measured after 48 h at room temperature. In the same way, when a solution of **5** in C₆D₆ was exposed to H₂S(g) a 50% of conversion to **4** was observed after 6 h. Compound [Rh(μ -SH)(CO)(PCy₃)₂] (**2**) behaves similarly although the transformation to **3** is much slower reaching 30% after a week in C₆D₆ at room temperature. In contrast, compound **1** is stable in solution under an argon atmosphere for a period of weeks with no detectable formation of the cluster [Rh₃(μ -H)(μ -S)₂{P(OPh)₃}₆].

Kinetic study and mechanism for the transformation of 4 into 5. In order to obtain relevant information for these transformations, the kinetics of the conversion of [Rh(μ -SH)(CO)(PPh₃)₂] (**4**) into [Rh₃(μ -H)(μ -S)₂(CO)₃(PPh₃)₃] (**5**) was studied by NMR spectroscopy in C₆D₆. Disappearance of **4** was monitored by ¹H NMR by integrating the SH resonances at δ -0.15 and -1.38 ppm, corresponding to *trans* and *cis* isomers, respectively, compared to the internal standard anisole. A typical plot of [**4**] vs *t* obtained from NMR measurements at [**4**]₀ = 0.035 M and 313.15 K is shown in Figure 5a. The 1/[**4**] vs *t* representation (Figure 5b) provided a linear fit that is representative of a second-order kinetic transformation with the slope of the line corresponding to the second-order rate constant *k* (Lmol⁻¹h⁻¹).^[23]

The temperature influence on the reaction rate was investigated in the temperature range 30-45 °C in C₆D₆. The rate constant was determined at four different temperatures (Table 5) and the overall activation parameters were determined using the logarithmic form of the Eyring equation:

$$\ln\left(\frac{k}{T}\right) = \ln\left(\frac{\kappa k_b}{h}\right) + \frac{\Delta S^\ddagger}{R} - \frac{\Delta H^\ddagger}{RT} \quad (1)$$

The kinetic parameters obtained from the Eyring plot (Figure 6) were $\Delta H^\ddagger = 24 \pm 3$ kJmol⁻¹ and $\Delta S^\ddagger = -233 \pm 8$ JK⁻¹mol⁻¹ ($\Delta G^\ddagger = 89 \pm 5$ kJmol⁻¹, 293.15 K). The large negative value of the entropy term suggests that the rate-determining step is of an associative nature.

A plausible multistep mechanism for the transformation of **4** into **5** is shown in Scheme 4 and outlined in the following set of equations. The first proposed step is the dimerization of **4** to give a tetranuclear intermediate, **C**, probably with a cubane-like structure (eq 2). The degradation of this intermediate species evolves to the hydrido trinuclear cluster **5** and a mononuclear species $[\text{Rh}(\text{SH})(\text{SH}_2)(\text{CO})(\text{PPh}_3)]$, **M** (eq 3). Finally, the reaction of **M** with **4** should result in the formation of **5** and the release of $\text{H}_2\text{S}(\text{g})$ (eq 4).

Kinetic calculations for the proposed mechanism were derived by assuming steady-state condition for species **C** and **M**. Although both species were not directly observed by spectroscopic means, its presence in a low concentration cannot be excluded as required by the steady-state approximation. The rate law obtained for this mechanism is presented in eq 5 and is in full agreement with the experimental second-order kinetic data.^[24]

$$-\frac{d[\text{4}]}{dt} = \left(\frac{3k_{1f}k_2}{k_{1r} + k_2} \right) [\text{4}]^2 \quad (5)$$

Although several sets of k_{1f} , k_{1r} and k_2 values could account for the k_{obs} at each temperature (eq 6), a kinetic analysis of this model using Berkeley-Madonna software allowed a rough estimation of the involved rate constants.^[25]

$$k_{\text{obs}} = \frac{3k_{1f}k_2}{k_{1r} + k_2} \quad (6)$$

The model parameters were estimated by visual fitting of the calculated $[\text{4}]$ vs t plot using numerical integration, and the experimental data. The obtained values: $k_{1f} \approx 10$, $k_{1r} \approx 8000$ and $k_2 \approx 1800$, suggest that the rate-determining step is the dimerization equilibrium leading to the assembly of the tetranuclear intermediate (**C**). The estimated equilibrium constant K (k_{1f}/k_{1r})

ranges between $0.9\text{--}1.2 \times 10^{-3}$ in the temperature range under study. Interestingly, the $\ln K$ vs $1/T$ plot gave a linear fit from which the following thermodynamic parameters were obtained: $\Delta H^\circ = 13 \text{ kJmol}^{-1}$ and $\Delta S^\circ = -14 \text{ JK}^{-1}\text{mol}^{-1}$ (See Supporting Information).

The formation of cubane-type sulfido clusters by dimerization of unsaturated sulfido-bridged dinuclear complexes resulting from the thermal loss of donor ligands has been described.^[26] In the same way, α -elimination of hydrogen chloride from hydrosulfido-bridge dinuclear complexes $[(\text{Cp}^*\text{MCl})_2(\mu_2\text{-SH})_2]$ results in the formation of a series of cubane-type sulfido clusters $[(\text{Cp}^*\text{M})_4(\mu_3\text{-S})_4]$ ($\text{M} = \text{Ru}, \text{Rh}, \text{Ir}$).^[11] However, the spontaneous dimerization of hydrosulfido-bridge dinuclear complexes has not been observed yet. Cubane-type clusters containing hydrosulfido ligands are rare although some examples having terminal hydrosulfido ligands are $[(\text{CpCr})_2\{\text{Fe}(\text{SH})\}_2(\mu_3\text{-S})_4]$ ^[27] and $[\{\text{Fe}(\text{SH})\}_4(\mu_3\text{-S})_4]$,^[28] that undergo condensation processes that lead to the formation of polycubane species. On the other hand, clusters having triply-bridging hydrosulfido ligands, $\mu_3\text{-SH}$, are rather scarce and only a few trinuclear complexes having the core $\text{M}_3(\mu_3\text{-SH})_2$ ($\text{M} = \text{Cu}, \text{Ag}$) have been structurally characterized.^[29] Closely related species to **C** are the cubano clusters $[\{\text{PtMe}_3\}_4(\mu_3\text{-SH})_4]$ ^[30] and $[\{\text{M}(\text{CO})_3\}_4(\mu_3\text{-SH})_4]$ ($\text{M} = \text{Mn}, \text{Re}$).^[31] In agreement with these observations, the short-lived species **C** could have a more complex and less symmetric tetranuclear structure involving hydrosulfido ligands with different coordination modes. In addition, the equilibrium involving **C** (eq 2) also explains the interconversion of the *trans* and *cis* isomers of **4**, which further support the participation of a cluster or polynuclear intermediate as **C** in the formation of **5** from **4**.

The transformation of **C** into **5** only requires the proton transfer between two neighbouring hydrosulfido ligands to give a polynuclear species containing a weakly bonded hydrogen sulfide ligand. This species probably breaks down into the trinuclear hydrosulfido-sulfido

intermediate $[\text{Rh}_3(\mu_3\text{-SH})(\mu_3\text{-S})(\text{CO})_3(\text{PPh}_3)_3]$, predecessor of **5** by intramolecular proton transfer, and the mononuclear species containing both hydrosulfido and hydrogensulfido ligands $[\text{Rh}(\text{SH})(\text{SH}_2)(\text{CO})(\text{PPh}_3)]$ (**M**). This species is a precursor of the unsaturated fragment $[\text{Rh}(\text{SH})(\text{CO})(\text{PPh}_3)]$ (14 electron species), due to the presence of the labile hydrogen sulfide ligand, and consequently, can be trapped by **4** to form a second equivalent of $[\text{Rh}_3(\mu_3\text{-SH})(\mu_3\text{-S})(\text{CO})_3(\text{PPh}_3)_3]$ with extrusion of $\text{H}_2\text{S}(\text{g})$. Transition metal complexes containing H_2S as ligand are also rare and limited to a few ruthenium mononuclear complexes^[32] which is agreement with the transient character of **M**. A related precedent of cluster formation with extrusion of $\text{H}_2\text{S}(\text{g})$ in Ir^{III} chemistry is the trinuclear cluster with an incomplete-cubane-type structure $[(\text{Cp}^*\text{Ir})_3(\mu_3\text{-S})(\mu_2\text{-S})(\mu_2\text{-SH})_2]$ which was obtained from the dinuclear tetra-hydrosulfido complex $[\text{Cp}^*\text{Ir}(\text{SH})_2(\mu_2\text{-SH})_2\text{Ir}(\text{SH})\text{Cp}^*]$.^[33] Further support for this proposal comes from the ability of bis-thiolato complexes as for example, $[\text{Rh}(\mu\text{-SPh})(\text{cod})]_2$, to form trinuclear aggregates $[\text{Rh}_3(\mu\text{-SPh})_2(\text{cod})_3]^+$ by reaction with unsaturated rhodium fragments “ $\text{Rh}(\text{cod})^{+}$ ”.^[34] Finally, as far as the transformation of $[\text{Rh}_3(\mu_3\text{-SH})(\mu_3\text{-S})(\text{CO})_3(\text{PPh}_3)_3]$ into **5** is concerned, it is worth mentioning that the hydrogen migration from metal to sulfur, with a switch from hydride to proton character, respectively, has been proposed in the DFT study of the catalytic activity of sulfido-bridged molybdenum clusters in hydrogenolysis of alkyl halides.^[35]

Concluding Remarks

Mononuclear acetylacetonate rhodium(I) complexes are convenient precursors for the synthesis of bis(hydrosulfido)-bridged dinuclear rhodium(I) complexes using $\text{H}_2\text{S}(\text{g})$ as hydrosulfido ligand source. The protonation of the acetylacetonate ligand by $\text{H}_2\text{S}(\text{g})$ in the complexes $[\text{Rh}(\text{acac})(\text{CO})(\text{PR}_3)]$ results in the formation of dinuclear complexes $[\text{Rh}(\mu\text{-$

$\text{SH})(\text{CO})(\text{PR}_3)_2$ and Hacac. Further deprotonation of a hydrosulfido ligand in $[\text{Rh}(\mu\text{-SH})(\text{CO})(\text{PR}_3)_2]$ by $[\text{Rh}(\text{acac})(\text{CO})(\text{PR}_3)]$ affords the trinuclear hydrido-sulfido clusters $[\text{Rh}_3(\mu\text{-H})(\mu_3\text{-S})_2(\text{CO})_3(\text{PR}_3)_3]$ through the trinuclear hydrosulfido-sulfido intermediates $[\text{Rh}_3(\mu_3\text{-SH})(\mu_3\text{-S})(\text{CO})_3(\text{PR}_3)_3]$ in a competitive process. Interestingly, the synthesis of both dinuclear $[\text{Rh}(\mu\text{-SH})(\text{CO})(\text{PR}_3)_2]$ and trinuclear $[\text{Rh}_3(\mu\text{-H})(\mu_3\text{-S})_2(\text{CO})_3(\text{PR}_3)_3]$ compounds can be accomplished by selecting the appropriate experimental conditions, in particular the $\text{H}_2\text{S}(\text{g})$ concentration in the reaction media. This behaviour probably accounts for the direct formation of $[\text{Rh}_3(\mu\text{-H})(\mu_3\text{-S})_2(\text{cod})_3]$ from $[\text{Rh}(\text{acac})(\text{cod})]$ and $\text{SH}_2(\text{g})$ because of the deprotonation of $[\text{Rh}(\mu\text{-SH})(\text{cod})]_2$ by $[\text{Rh}(\text{acac})(\text{cod})]$ is faster than their formation from $\text{H}_2\text{S}(\text{g})$.

In contrast with the dinuclear complex $[\text{Rh}(\mu\text{-SH})(\text{P}\{\text{OPh}\}_3)_2]_2$, that is stable both in solution and in the solid state, the complexes $[\text{Rh}(\mu\text{-SH})(\text{CO})(\text{PR}_3)_2]$ slowly transform in solution to trinuclear hydrido-sulfido clusters $[\text{Rh}_3(\mu\text{-H})(\mu_3\text{-S})_2(\text{CO})_3(\text{PR}_3)_3]$ with the release of $\text{H}_2\text{S}(\text{g})$. This spontaneous transformation, that is reversible in the presence of $\text{H}_2\text{S}(\text{g})$, follows a second-order kinetic in benzene. The determination of the activation parameters for this process strongly suggests a multistep mechanism involving the formation of a hydrosulfido tetranuclear intermediate resulting from the dimerization of two dinuclear $[\text{Rh}(\mu\text{-SH})(\text{CO})(\text{PR}_3)_2]$ complexes as the rate-determining step. This chemical behaviour is driven by the outstanding stability of the trinuclear hydrido-sulfido clusters that are a thermodynamic sink in this chemistry.

Experimental Section

General Methods All manipulations were performed under a dry argon atmosphere using Schlenk-tube techniques. Solvents were dried by standard methods and distilled under argon immediately prior to use. ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded on a Varian Gemini 300 (300.08 and 121.47 MHz) and Bruker Avance 300 (300.13 and 121.50 MHz) spectrometers. Chemical shifts are reported in parts per million and referenced to SiMe_4 using the signal of the deuterated solvent (^1H) and 85% H_3PO_4 (^{31}P) 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. The initial choice of chemical shifts and coupling constants were optimized by successive iterations following a standard least-squares procedure, a numerical assignment of the experimental frequencies was used. IR spectra were recorded in solution on a Perkin-Elmer Spectrum One spectrometer using a cell with NaCl windows. Molecular weights were determined with a Knauer osmometer using chloroform solutions of the complexes. Elemental C, H and N analysis were performed in a Perkin-Elmer 2400 CHNS/O microanalyzer. Mass spectra were recorded in a VG Autospec double-focusing mass spectrometer operating in the FAB^+ mode. Ions were produced with the standard Cs^+ gun at ca. 30 Kv, 3-nitrobenzyl alcohol (NBA) was used as matrix. Electrospray mass spectra (ESI-MS) were recorded on a Bruker MicroTof-Q using sodium formate as reference. $[\text{Rh}(\text{acac})\{\text{P}(\text{OPh})_3\}_2]$,^[36] and $[\text{Rh}(\text{acac})(\text{CO})(\text{PR}_3)]$ (R = Ph, Cy)^[37] were prepared according to literature methods. $\text{H}_2\text{S}(\text{g})$ was obtained commercially and used without further purification.

Synthesis of $[\text{Rh}(\mu\text{-SH})\{\text{P}(\text{OPh})_3\}_2]_2$ (1). A solution of $[\text{Rh}(\text{acac})\{\text{P}(\text{OPh})_3\}_2]$ (0.800 g, 0.972 mmol) in diethyl ether (40 mL) was stirred for 2 hours under a H_2S (g) atmosphere at 273 K to give a yellowish suspension. The solvent was evaporated to dryness, and the residue

washed with n-hexane (3 x 10 mL) and dried under vacuum to give a pale-yellow solid (0.690 g, 94 %). ^1H NMR (300.08 MHz, C_6D_6 , 293 K): δ = 7.30 (d, 24 H), 6.96 (t, 24 H), 6.77 (t, 12 H) (OPh), 0.47 (s, 2H; SH); $^{31}\text{P}\{^1\text{H}\}$ NMR (121.47 MHz, C_6D_6 , 293 K): δ = 117.8 (dm, $J(\text{Rh},\text{P}) = 283$ Hz); MS (FAB+, CH_2Cl_2): m/z (%): 1512 (10) $[\text{M}]^+$, 1168 (45) $[\text{M} - \text{SH}_2 - \text{P}(\text{OPh})_3]^+$, 890 (45) $[\text{M} - 2\text{H} - 2\text{P}(\text{OPh})_3]^+$, 858 (100) $[\text{M} - \text{SH}_2 - 2\text{P}(\text{OPh})_3]^+$, 580 (85) $[\text{M} - 2\text{H} - 3\text{P}(\text{OPh})_3]^+$; MS (FAB-, CH_2Cl_2): m/z (%): 1510 (45) $[\text{M} - 2\text{H}]^-$, 1200 (10) $[\text{M} - \text{H} - \text{P}(\text{OPh})_3]^-$, 890 (15) $[\text{M} - 2\text{H} - 2\text{P}(\text{OPh})_3]^-$; mol. weight calcd 1513, found: 1500; elemental analysis calcd (%) for $\text{C}_{72}\text{H}_{62}\text{O}_{12}\text{P}_4\text{Rh}_2\text{S}_2$ (1513.10): C 57.15, H 4.13, S 4.24; found: C 57.13, H 3.99, S 4.39.

Synthesis of $[\text{Rh}(\mu\text{-SH})(\text{CO})(\text{PCy}_3)]_2$ (2). A suspension of $[\text{Rh}(\text{acac})(\text{CO})(\text{PCy}_3)]$ (0.250 g, 0.490 mmol) in tetrahydrofuran (2 mL) was stirred for 24 hours under a H_2S (g) atmosphere at room temperature to give a bright orange-red suspension. The suspension was cooled to 258 K and the solid collected by filtration, washed with cold tetrahydrofuran (1 mL) and dried under vacuum (0.083 g, 38 %). ^1H NMR (300.08 MHz, CDCl_3 , 293 K): δ = 2.23-1.85 (set of m, 18H), 1.85-1.40 (set of m, 32H), 1.23 (m, 16H) (Cy), -0.58 (t, $^3J(\text{H},\text{P}) = 3.3$ Hz, 2H; SH); $^{31}\text{P}\{^1\text{H}\}$ NMR (121.47 MHz, CDCl_3 , 293 K): δ = 51.43 (dm, $J(\text{Rh},\text{P}) = 156$ Hz); MS (ESI+, THF/ CH_3CN): m/z (%): 911.2 $[\text{M} + \text{Na}]^+$; IR (CH_2Cl_2): $\nu = 1949$ cm^{-1} (s) (CO); elemental analysis calcd (%) for $\text{C}_{38}\text{H}_{68}\text{O}_2\text{P}_2\text{Rh}_2\text{S}_2$ (888.83): C 51.35, H 7.71, S 7.21; found: C 51.34, H 7.91, S 7.53.

Synthesis of $[\text{Rh}_3(\mu\text{-H})(\mu_3\text{-S})_2(\text{CO})_3(\text{PCy}_3)_3]$ (3). A solution of $[\text{Rh}(\text{acac})(\text{CO})(\text{PCy}_3)]$ (0.150 g, 0.294 mmol) in dichloromethane (10 mL) was stirred for 1 hour under a H_2S (g) atmosphere at room temperature to give a red solution. The solvent was removed under vacuum and the residue dissolved in diethyl ether (5 mL). The stirring of the solution induced the crystallization of the compound as orange-red microcrystals. The suspension was

concentrated and cooled to 258 K. The solid was collected by filtration, washed with cold diethyl ether and then vacuum-dried (0.089 g, 70 %). ^1H NMR (300.08 MHz, CDCl_3 , 293 K): δ = 2.34 (m, 2H), 2.27-1.82 (set of m, 24 H), 1.81-1.61 (set of m, 27 H), 1.60-1.39 (set of m, 18 H), 1.23(m, 28H) (Cy), -14.33 (tt, $J(\text{Rh},\text{H})$ = 31 Hz, $^2J(\text{P},\text{H})$ = 3.3 Hz, 1H; Rh-H); MS (ESI-, THF/ CH_3CN): m/z (%): 1297.3 $[\text{M} - \text{H}]^-$; IR (CH_2Cl_2): ν = 1983 (w), 1963 (s) and 1934 cm^{-1} (s) (CO); elemental analysis calcd (%) for $\text{C}_{57}\text{H}_{100}\text{O}_3\text{P}_3\text{Rh}_3\text{S}_2$ (1299.18): C 52.70, H 7.76, S 4.93; found: C 52.97, H 7.23, S 4.71.

Synthesis of $[\text{Rh}(\mu\text{-SH})(\text{CO})(\text{PPh}_3)]_2$ (4). A Schlenk tube charged with $[\text{Rh}(\text{acac})(\text{CO})(\text{PPh}_3)]$ (0.250 g, 0.508 mmol) and tetrahydrofuran (2 mL) was cooled at 195 K, evacuated and connected to a balloon of $\text{H}_2\text{S}(\text{g})$. The mixture was stirred at 195 K for 10 min. and then at room temperature for 4 hours to give a bright yellow suspension. The crystallization was completed by addition of pentane (8 mL). The suspension was cooled to 258 K and the solid collected by filtration, washed with cold pentane (4 mL) and dried under vacuum (0.178 g, 82 %). The compound was isolated as the *trans* (**4a**, 92%) and *cis* (**4b**, 8%) isomers. ^1H NMR (300.08 MHz, C_6D_6 , 293 K): δ = 7.85 (tm, 12 H), 7.01 (m, 18 H) (Ph), -0.15 (m, 2H, $^3J(\text{P},\text{H})$ = 5.5 Hz, $^3J(\text{P}-\text{H})$ = 2.8 Hz, $^2J(\text{Rh},\text{H})$ = 2.8 Hz, SH) (**4a**, *trans* isomer), 7.6 (ddm, 12 H), 6.90 (m, 18 H) (Ph), -1.38 (t, 1H, $^3J(\text{P},\text{H})$ = 6.5 Hz, SH), -1.39 (t, 1H, $^3J(\text{P},\text{H})$ = 6.5 Hz, SH) (**4b**, *cis* isomer); $^{31}\text{P}\{^1\text{H}\}$ NMR (121.47 MHz, C_6D_6 , 293 K): δ = 42.11 (d, $J(\text{Rh},\text{P})$ = 162 Hz) (**4a**, *trans* isomer), 41.38 (d, $J(\text{Rh},\text{P})$ = 161 Hz), (**4b**, *cis* isomer); MS (FAB+, toluene): m/z (%): 852 (20) $[\text{M}]^+$, 824 (20) $[\text{M} - \text{CO}]^+$, 794 (35) $[\text{M} - 2\text{CO} - 2\text{H}]^+$; IR (CH_2Cl_2): ν = 1972 cm^{-1} (s) (CO); elemental analysis calcd (%) for $\text{C}_{38}\text{H}_{32}\text{O}_2\text{P}_2\text{Rh}_2\text{S}_2$ (852.55): C 53.54, H 3.78, S 7.52; found: C 53.77, H 3.73, S 7.76.

Synthesis of $[\text{Rh}_3(\mu\text{-H})(\mu_3\text{-S})_2(\text{CO})_3(\text{PPh}_3)_3]$ (5). *Method A.* A solution of $[\text{Rh}(\text{acac})(\text{CO})(\text{PPh}_3)]$ (0.150 g, 0.305 mmol) in dichloromethane (8 mL) was stirred for 1

hour under a H₂S (g)/Ar (g) (1:1) atmosphere at room temperature to give a red solution. The solvent was removed under vacuum and the residue dissolved in diethyl ether (20 mL). Addition of n-hexane (5 mL) gave a brown solid that was filtered-off. Concentration of the resulting orange solution and addition of n-hexane (5 mL) afforded the compound as red-violet microcrystals which were collected by filtration, washed with cold n-hexane and dried under vacuum (0.086 g, 68%). *Method B.* [Rh(μ -SH)(CO)(PPh₃)₂] (0.114 g, 0.134 mmol) and [Rh(acac)(CO)(PPh₃)] (0.066 g, 0.134 mmol) were reacted in dichloromethane (15 mL) for one hour to give a deep red solution. The solvent was removed under vacuum and the residue extracted with diethyl ether and then filtered to give an orange solution. Work up as described before gave the compound as red-violet microcrystals (0.116 g, 70 %). *Method C.* A solution of [Rh(μ -SH)(CO)(PPh₃)₂] (0.100 g, 0.117 mmol) in toluene (5 mL) was heated at 333 K for 2 hours to give a violet solution. Work up as described in method B gave the compound as red-violet microcrystals (0.068 g, 70 %). ¹H NMR (300.08 MHz, C₆D₆, 293 K): δ = 8.01 (m, 18H), 7.34-7.20 (m, 27H) (Ph), -13.90 (tt, 1H, J (Rh,H) = 31 Hz, 2J (P,H) = 3 Hz); MS (FAB-, toluene): m/z (%): 1243 (100%) [M – H][–]; MS (FAB+, toluene): m/z (%): 1159 (15) [M – H – 3CO]⁺, 953 (28) [M – H – PPh₃ – CO]⁺, 925 (30) [M – H – PPh₃ – 2CO]⁺, 897 (30) [M – H – PPh₃ – 3CO]⁺; IR (CH₂Cl₂): ν = 2006 (sh), 1988 (s), and 1961 cm^{–1} (s) (CO); elemental analysis calcd (%) for C₅₇H₄₆O₃P₃Rh₃S₂ (1244.75): C 55.00, H 3.72, S 5.15; found: C 54.97, H 3.87, S 5.31.

Kinetic measurements. The rate of conversion of **4** to **5** was measured by ¹H NMR spectroscopy. A 5 mm NMR tube containing a C₆D₆ solution of **4** (0.035 M) and methoxybenzene (1 μ L) was introduced into the NMR probe preheated to the desired temperature (35 – 50 °C). After allowing for thermal equilibration and experiment setup periodic NMR spectra (typically each 10 min) with identical acquisition parameters were

recorded over several hours. Disappearance of **4** was monitored by ^1H NMR spectroscopy by integrating the proton resonances of the hydrosulfido ligands compared to the internal standard methoxybenzene using automatic integration software. The observed rate constants for consumption of **4** were obtained from linear least-square regression analysis. The experimental data were fitted to a four-parameter model using Berkeley Madonna 8.0.1 software.^[25] The model parameters were estimated by visual fitting of the simulated curves to the experimental data using the software package. Integration was performed using the fourth-order Runge-Kutta method.

The activation parameters, $\Delta H^\ddagger$ and $\Delta S^\ddagger$, were calculated from a linear least-squares fit of $\ln(k/T)$ vs $1/T$ (Eyring equation). The uncertainties in $\Delta H^\ddagger$ and $\Delta S^\ddagger$ were computed from the error propagation formulas derived from the Eyring equation by Girolami and co-workers.^[38] The total uncertainty in the determination of k was assumed to be 5%.^[39] The estimated uncertainty in the temperature measurements was 1K.

Crystal Structure Determination of $[\text{Rh}(\mu\text{-SH})\{\text{P}(\text{OPh})_3\}_2]_2$ (1**) and $[\text{Rh}_3(\mu\text{-H})(\mu_3\text{-S})_2(\text{CO})_3(\text{PCy}_3)_3]$ (**3**).** A summary of crystal data, data collection and refinement parameters are given in Table 4. Selected crystals were mounted on a Bruker SMART CCD three-circle diffractometer equipped with a graphite monochromator. In the case of **3**, most of the crystals showed a twinned nature; eventually a tiny weakly diffracting and slightly twinned sample, was selected after several trials. Data collection was performed at low temperature (100(2) K) using Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). A semiempirical absorption correction was applied using SADABS program, as implemented in SAINT-PLUS package.^[40] Both structures were solved by Patterson methods using the program SHELXS-97, completed by subsequent difference Fourier techniques, and refined by full matrix least-squares on F^2 with SHELXL-97.^[41] All non-disordered non-hydrogen atoms were refined with anisotropic displacement

parameters. A static disorder was identified in the crystal structure of **1** affecting a phenyl group and was modelled with the splitting of three carbon atoms. In the case of **3**, a toluene molecule was heavily disordered around a centre of symmetry; this was included in the refinement with an occupancy of 0.5. Hydrogens were included in both structures for all non-disordered carbon atoms from observed (**1**) or calculated (**3**) positions; in both cases a riding refinement was applied. In **3**, the hydride position was calculated from a minimization of the potential electrostatic energy once the whole molecule was refined (HYDEX program).^[42]

CCDC-743620 (**1**) and CCDC-743621 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Figure and Scheme legends

Figure 1. Molecular structure of $[\text{Rh}(\mu\text{-SH})\{\text{P}(\text{OPh})_3\}_2]_2$ (**1**) (Only hydrogens bonded to S atoms have been represented for clarity).

Figure 2. Experimental and simulated ^1H NMR of **4** (SH region) in C_6D_6 .

Figure 3. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **5** at 253 K in $[\text{D}_8]$ -toluene: experimental (a) and simulated (b).

Figure 4. Molecular structure of $[\text{Rh}_3(\mu\text{-H})(\mu_3\text{-S})_2(\text{CO})_3(\text{PCy}_3)_3]$ (**3**) (The bridging hydride has been represented as H(2)).

Figure 5. a) Decay of **[4]** vs time for the conversion of **4** into **5** in C_6D_6 at 313.15 K determined from ^1H NMR measurements ($[\text{4}]_0 = 0.035 \text{ mol L}^{-1}$). b) Second-order kinetic fit of the data: $1/[\text{4}]$ vs time plot.

Figure 6. Eyring plot for the conversion of **4** into **5** in C₆D₆. The line represents the least-square fit to the data point.

Scheme 1. Synthesis of bis(hydrosulfido)-bridged dinuclear complexes and trinuclear hydrido-sulfido clusters.

Scheme 2. Formation of trinuclear hydrido-sulfido clusters from bis(hydrosulfido)-bridged dinuclear complexes.

Scheme 3. $\text{H}_2\text{S}(\text{g})$ mediated conversion between bis(hydrosulfido)-bridged dinuclear complexes and trinuclear hydrido-sulfido clusters.

Scheme 4. Proposed mechanism for the transformation of **4** into **5**.

Table 1. $^{31}\text{P}\{^1\text{H}\}$ NMR data (calculated spectra) for compounds $[\text{Rh}_3(\mu\text{-H})(\mu_3\text{-S})_2(\text{CO})_3(\text{PR}_3)_3]$ (**3**, CDCl_3 , RT; **5**, $[\text{D}_8]\text{-toluene}$, 253 K) $[\text{Rh}_3(\mu\text{-H})(\mu_3\text{-S})_2(\text{CO})_3(\text{PCy}_3)_3]$ (**3**)

	δ (ppm)		$J_{\text{Rh-P}}$ (Hz)	$J_{\text{P-P}}$ (Hz)
P_A	48.88	dt	149.0	6.5 ($\text{P}_\text{A}\text{-P}_\text{B}$)
P_B	44.57	dt	141.0	5.1 ($\text{P}_\text{B}\text{-P}_\text{C}$)
P_C	43.81	ddd	152.0	8.3 ($\text{P}_\text{C}\text{-P}_\text{A}$)

 $[\text{Rh}_3(\mu\text{-H})(\mu_3\text{-S})_2(\text{CO})_3(\text{PPh}_3)_3]$ (**5**)

	δ (ppm)		$J_{\text{Rh-P}}$ (Hz)	$J_{\text{P-P}}$ (Hz)
P_C	34.47	ddd	156.4	15.0 ($\text{P}_\text{C}\text{-P}_\text{A}$)
P_A	34.12	dt	148.5	10.5 ($\text{P}_\text{A}\text{-P}_\text{B}$)
P_B	32.37	ddd	148.4	3.5 ($\text{P}_\text{B}\text{-P}_\text{C}$)

Table 2. Selected bond distances (Å) and angles (°) for complex $[\text{Rh}(\mu\text{-SH})\{\text{P}(\text{OPh})_3\}_2]_2$ (**1**).

Rh(1)-S(1)	2.3665(11)	Rh(2)-S(1)	2.3521(12)
Rh(1)-S(2)	2.3617(11)	Rh(2)-S(2)	2.3618(11)
Rh(1)-P(1)	2.1691(12)	Rh(2)-P(3)	2.1544(12)
Rh(1)-P(2)	2.1634(12)	Rh(2)-P(4)	2.1618(12)
P(1)-O(1)	1.622(3)	P(2)-O(4)	1.611(3)
P(1)-O(2)	1.612(3)	P(2)-O(5)	1.611(3)
P(1)-O(3)	1.620(3)	P(2)-O(6)	1.620(3)
S(1)-Rh(1)-S(2)	78.22(4)	S(1)-Rh(2)-S(2)	78.50(4)

S(1)-Rh(1)-P(1)	94.43(4)	S(1)-Rh(2)-P(3)	91.45(5)
S(1)-Rh(1)-P(2)	167.48(4)	S(1)-Rh(2)-P(4)	173.39(5)
S(2)-Rh(1)-P(1)	172.07(5)	S(2)-Rh(2)-P(3)	166.75(5)
S(2)-Rh(1)-P(2)	92.84(4)	S(2)-Rh(2)-P(4)	96.78(4)
P(1)-Rh(1)-P(2)	93.94(4)	P(3)-Rh(2)-P(4)	92.48(5)
Rh(1)-S(1)-Rh(2)	87.01(4)	Rh(1)-S(2)-Rh(2)	86.90(4)
Rh(1)-P-O (mean)	118.46(5)	Rh(2)-P-O (mean)	117.55(5)

Table 3. Selected bond distances (Å) and angles (°) for the trinuclear complex $[\text{Rh}_3(\mu\text{-H})(\mu_3\text{-S})_2(\text{CO})_3(\text{PCy}_3)_3]$ (**3**).

Rh(1)-Rh(3)	2.8418(11)	Rh(3)···Rh(2)	3.0900(11)
Rh(1)-P(1)	2.315(3)	Rh(3)-P(3)	2.311(3)
Rh(1)-S(1)	2.364(2)	Rh(3)-S(1)	2.365(2)
Rh(1)-S(2)	2.364(2)	Rh(3)-S(2)	2.372(2)
Rh(1)-C(55)	1.836(10)	Rh(3)-C(57)	1.841(11)
O(1)-C(55)	1.153(10)	O(3)-C(57)	1.167(12)
Rh(2)-P(2)	2.291(2)	Rh(2)···Rh(1)	3.2681(11)
Rh(2)-S(1)	2.336(2)	Rh(2)-S(2)	2.333(2)
Rh(2)-C(56)	1.816(11)	O(2)-C(56)	1.160(11)
P(1)-Rh(1)-S(1)	175.99(9)	P(3)-Rh(3)-S(1)	92.86(9)
P(1)-Rh(1)-S(2)	94.77(8)	P(3)-Rh(3)-S(2)	173.03(9)
P(1)-Rh(1)-C(55)	91.9(3)	P(3)-Rh(3)-C(57)	95.0(3)
S(1)-Rh(1)-S(2)	81.40(8)	S(1)-Rh(3)-S(2)	81.22(8)
S(1)-Rh(1)-C(55)	92.0(3)	S(1)-Rh(3)-C(57)	172.2(3)
S(2)-Rh(1)-C(55)	172.8(3)	S(2)-Rh(3)-C(57)	91.0(3)
Rh(1)-S(1)-Rh(2)	88.11(8)	Rh(1)-S(2)-Rh(2)	88.18(8)
Rh(1)-S(1)-Rh(3)	73.88(7)	Rh(1)-S(2)-Rh(3)	73.74(7)
Rh(2)-S(1)-Rh(3)	82.20(8)	Rh(2)-S(2)-Rh(3)	82.10(8)

P(2)-Rh(2)-S(1)	167.33(10)	Rh(1)-C(55)-O(1)	173.7(9)
P(2)-Rh(2)-S(2)	93.51(8)	Rh(2)-C(56)-O(2)	176.6(9)
P(2)-Rh(2)-C(56)	91.4(3)	Rh(3)-C(57)-O(3)	177.5(9)
S(1)-Rh(2)-S(2)	82.66(8)	Rh(1)-P(1)-C(mean)	113.0(2)
S(1)-Rh(2)-C(56)	92.9(3)	Rh(2)-P(2)-C(mean)	113.4(2)
S(2)-Rh(2)-C(56)	174.7(3)	Rh(3)-P(3)-C(mean)	113.1(2)

Table 4. Selected crystal parameters and refinement data for complexes **1** and **3**.

	1	3
formula	C ₇₂ H ₆₂ O ₁₂ P ₄ Rh ₂ S ₂	C ₅₇ H ₁₀₀ O ₃ P ₃ Rh ₃ S ₂ · 1.5 C ₇ H ₈
crystal system	triclinic	monoclinic
space group	<i>P</i> -1	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> [Å]	13.8202(8)	17.950(2)
<i>b</i> [Å]	14.1809(8)	13.5996(17)
<i>c</i> [Å]	18.8312(11)	28.278(4)
α [°]	97.0990(10)	90.0
β [°]	95.5630(10)	96.058(3)
γ [°]	113.5980(10)	90.0
<i>V</i> [Å ³], <i>Z</i>	3312.3(3), 2	6864.5(15), 4
<i>M</i> [g mol ⁻¹]	1513.04	1437.33
ρ [g cm ⁻³]	1.517	1.391
θ range [°]	2.09 – 28.77	1.66 – 24.90
μ [mm ⁻¹]	0.721	0.886
measured reflns	41128	31214
Independent reflns	15714	11693
Observed reflns (<i>I</i> > 2 σ (<i>I</i>))	7986	8219
Refined param. / constraints	882 / 0	701 / 2
<i>R</i> ₁ / <i>wR</i> ₂ (<i>F</i> ² > 2 σ (<i>F</i> ²))	0.0514 / 0.0645	0.0868 / 0.1596
<i>R</i> ₁ / <i>wR</i> ₂ (all data)	0.0998 / 0.0719	0.1276 / 0.1755

Table 5. Temperature dependence of the second-order observed rate constant, k_{obs} , for the conversion of **4** into **5**, in C_6D_6 .

T/K	$k_{\text{obs}} \times 10^3 / \text{Lmol}^{-1} \text{s}^{-1}$	R^2
303.15	0.993 ± 0.002	0.999
308.15	1.22 ± 0.01	0.999
313.15	1.45 ± 0.01	0.997
318.15	1.63 ± 0.01	0.999

^a Correlation coefficient

Text for the Table of Contents

New precursors for sulfido clusters:

Bis-(hydrosulfido)-bridged dinuclear rhodium(I) compounds and trinuclear hydrido-sulfido clusters are accessible from rhodium(I) acetylacetonate complexes and $\text{H}_2\text{S(g)}$. The complexes $[\text{Rh}(\mu\text{-SH})(\text{CO})(\text{PR}_3)]_2$ slowly transform into the clusters $[\text{Rh}_3(\mu\text{-H})(\mu_3\text{-S})_2(\text{CO})_3(\text{PR}_3)_3]$ with the release of $\text{H}_2\text{S(g)}$ in a reversible way. This transformation follows a second-order type kinetics.

Jesús J. Pérez-Torrente, M. Victoria Jiménez, Marc A. F. Hernandez-Gruel, María J. Fabra, Fernando J. Lahoz and Luis A. Oro* Page – Page*

On the Synthesis and Chemical Behaviour of the Elusive Bis(hydrosulfido)-bridged Dinuclear Rhodium(I) Complexes $[\text{Rh}(\mu\text{-SH})(\text{CO})(\text{PR}_3)]_2$

Keywords: Sulfido clusters • dinuclear complexes • rhodium • hydrosulfido • sulfido