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Bonding isomerism in the η^1-P coordination of the P_4X_3 (X = S, Se) molecules toward 16e rhodium fragments stabilized by tripodal tetradentate ligands

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Abstract

The reaction of tetraphosphorus trichalcogenides P_4X_3 (X = S, Se) with the electronically and coordinatively unsaturated 16 electron systems $[(EP_3)Rh]^+$ [E = N, NP_3 = tris(2-diphenylphosphanylethyl)amine, (**1**); E = P, PP_3 = tris(2-diphenylphosphanylethyl)phosphane, (**2**)] in tetrahydrofuran affords new tetraphosphorus trichalcogenide derivatives of formula $[(EP_3)Rh(P_4X_3)]CF_3SO_3$ [E = N; X = Se (**3**), S (**5**). E = P; X = Se (**4**), S (**6**)]. In the P_4Se_3 derivatives **3** and **4** the heptatomic cage is bound to the metal through the apical phosphorus atom. The P_4S_3 derivatives **5** and **6** are obtained as pairs of coordination isomers, with the cage linked to the metal either through the apical or through one of the basal P atoms; the former isomer is predominant and its amount depends on the nature of the *trans*-disposed apical donor (N or P) of the tripodal ligand. The monometal species $[(NP_3)Rh(\eta^1\text{-}P_4S_3)]CF_3SO_3$ (**5**) reacts with **1** affording the dimetal compound $[\{(NP_3)Rh\}_2(\mu, \eta^{1:1}\text{-}P_{apical},\text{-}P_{basal}\text{-}P_4S_3)](CF_3SO_3)_2$, where the cage exhibits both modes of bonding. All of the compounds have been characterized by ^{31}P NMR spectra and elemental analyses.

Keywords: Rhodium complexes; Tetradentate tripodal ligands; Tetraphosphorustrichalcogenides; ^{31}P NMR spectra

1. Introduction

The mixed cage molecules E_4X_3 (E = P, As; X = S, Se) (Scheme 1, **I**) possess a unique structure exhibiting a pseudotetrahedral array of pnicogen atoms, where a homocyclic-E_3 unit is connected via three bridging chalcogen atoms to a single pnicogen in apical position [1]. The behaviour of such molecules towards transition metal fragments has been widely studied and a variety of compounds containing units which originate from the disruptive fragmentation of the heptatomic cages, particularly P_4S_3 and As_4S_3, have been described [2–7]. Very often the reactions proceed through complicated multistep thermal and/or photochemical degradation and aggregation to form metal complexes, mostly in low yield, containing E_mX_n groups for which the original cage topology is no longer evident [8]. Among the numerous compounds originating from these processes there are complexes which may be formally considered as resulting from the initial interaction of the metal fragment with the intact molecule, followed by stepwise disruption of P–P and/or P–X bonds (Scheme 1 **II**–**IV**) [9–11].

Nevertheless the primary complexation of the cages has been described in a few instances and, until recently, it had been accomplished through the apical phosphorus [12,13]. Only very recently rhenium complexes have been described which contain the intact cage bound to the metal through either the apical or one of the basal P atoms, the latter being predominant [14]. Soon thereafter, polymeric weakly coordinated silver–P_4S_3 adducts in which the intact cage interacts with the metal through one sulfur and both the apical and one basal P atoms have been reported [15]. Due to the several potential coordination sites, to the E–E and E–X reactive edges as

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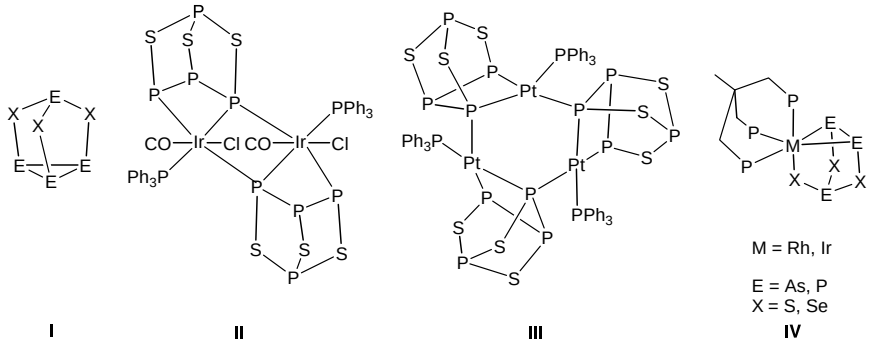


Scheme 1.

well as to the faces of different geometries exhibited by such *closo*-molecules, the course of the reaction of P_4X_3 with metal fragments is always difficult to be predicted. In part this is due to the small number of stable complexes containing the intact molecules; furthermore, these complexes are either poorly soluble [10,12] or too reactive to be isolated and characterized by standard techniques [15]. Hence, systematic studies aimed at gaining insight into the factors favouring the coordination and the specific activation modes of such complexes are sparse and worth to be further expanded.

In continuing our research activity in this field, we have investigated the reactivity of P_4X_3 (X = S, Se) towards coordinatively and electronically unsaturated trigonal pyramidal rhodium fragments, stabilized by tripodal tetradentate ligands, which are known to be excellent precursors for the activation of H–H, C–H, [16] S–H [17] as well as P–P bonds in the P_4 molecule [18]. Thus, the $[(EP_3)Rh]^+$ [E = N (**1**) and P (**2**)] species react with P_4X_3 yielding adducts of formula $[(EP_3)Rh(\eta^1\text{-}P_4X_3)]CF_3SO_3$ [E = N; X = Se (**3**), S (**5**). E = P; X = Se (**4**), S (**6**)]. Remarkably, while P_4Se_3 derivative solutions contain the intact cage bound to the metal fragment through the apical P atom, the P_4S_3 compounds exhibit a mixture of Rh-η^1-P_{apical} and Rh-η^1-P_{basal} coordination isomers, the former being predominant. All of the compounds have been characterized by $^{31}P\{^1H\}$ NMR measurements. The monometal species $[(NP_3)Rh(\eta^1\text{-}P_4S_3)]CF_3SO_3$ (**5**) affords with $[(NP_3)Rh]^+$ (**1**) a dinuclear compound of formula $[\{(NP_3)Rh\}_2(P_4S_3)](CF_3SO_3)_2$ (**7**) which combines the Rh-η^1-P_{apical} and Rh-η^1-P_{basal} coordination modes. A preliminary account on these compounds has been given [19].

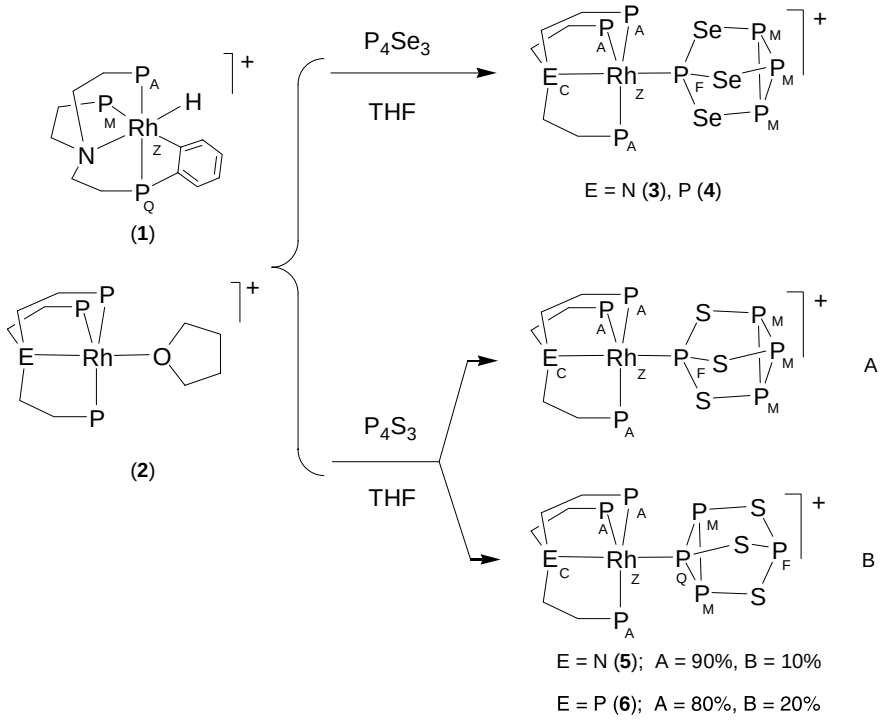
2. Results and discussion

The rhodium fragments **1** and **2**, Scheme 2, which form by electrophilic attack of CF_3SO_3Me on the hydride complexes $[(EP_3)RhH]$ in THF following methane elimination [E = N, NP_3 = tris(2-diphenylphosphanylethyl)amine; E = P, PP_3 = tris(2-diphenylphosphanylethyl)phosphane] [16], react promptly at room temperature with the stoichiometric amount of P_4X_3 (X = S, Se) in toluene to yield, after workup, brown microcrystals of formula $[(EP_3)Rh(P_4X_3)]CF_3SO_3$ [E = N, X = Se, (**3**), S (**5**); E = P, X = Se (**4**), S (**6**)].

The P_4S_3 derivatives are obtained in fairly higher yield than the P_4Se_3 ones (see Section 3). The solids are stable under inert atmosphere and may be handled in the air for a limited time; they are soluble in deoxygenated CH_2Cl_2, THF and $(CH_3)_2CO$ and the solutions are stable up to ≈45 °C, at higher temperatures they decompose unspecifically providing very complicated ^{31}P NMR spectra which denied simple analysis. The elemental analysis confirms the formation of 1:1 adducts between the $[(EP_3)Rh]^+$ (**1**, **2**) synthon and the P_4X_3 molecule. The formation of the compounds is sketched in Scheme 2, where the labelling scheme used for the different phosphorus nuclei is also defined. The compounds have been characterized by $^{31}P\{^1H\}$ NMR measurements. The NMR data are collected in Table 1 where the data of the uncoordinated P_4X_3 cages are provided for comparison. The intensity ratios of the $^{31}P\{^1H\}$ signals are in accordance with the proposed formulae.

2.1. ^{31}P NMR characterization of the P_4Se_3 coordination compounds

The $^{31}P\{^1H\}$ NMR spectrum of the tetraphosphorus triselenide **4** consists of a first-order A_3CFM_3Z splitting pattern that yields a quartet for the apical phosphorus (P_C) of the tripodal PP_3 ligand and a doublet for the three terminal atoms (P_A); both signals are twice doubled by coupling with the rhodium and with the apical P_F of the cage. The four phosphorus atoms of the heptatomic cage forms the FM_3 part of the spin system (Table 1). The apical P_4Se_3 phosphorus atom, P_F, which couples with all the eight NMR active nuclei of the complex cation, yields a weak multiplet which is markedly downfield shifted with respect to the free molecule. The three magnetically equivalent P_M atoms exhibit a



Scheme 2.

doublet due to the coupling with P_F and their chemical shift is only marginally affected by coordination. The PP_3Rh fragment has chemical shifts and coupling constants that parallel those reported for several trigonal bipyramidal rhodium(I) complexes with coligands such as P_4, [18] CO, PPh_3 [16] and XH (X = S, Se, Te) [17] in the fifth position. In addition the cage presents NMR parameters in the range of those observed for the [(triphos)$Re(CO)_2(\eta^1$-P_{apical}-$P_4Se_3)]CF_3SO_3$ complex which is the only solution characterized compound containing the intact cage bound to the metal through the apical P atom, although such isomer formed in low amount [14]. The same coordination geometry consistent with a trigonal bipyramidal geometry around the rhodium(I) and the intact cage bound through the apical P atom, may be safely assigned to the NP_3 derivative **3** that exhibits an A_3FM_3Z spin system in the $^{31}P\{^1H\}$ NMR spectrum in accordance with the presence of the NMR inactive nitrogen in the apical position of the tripodal ligand. The $^{31}P\{^1H\}$ NMR spectra of the complexes **3** and **4** do not change with the temperature in the range investigated (from −50 to +40, experiment in a sealed NMR tube) which allows to exclude dynamic behaviour. Due to the limited solubility of the compounds ^{77}Se NMR spectra were not recorded.

2.2. ^{31}P NMR characterization of the P_4S_3 coordination compounds

The $^{31}P\{^1H\}$ NMR spectra of the $[(EP_3)Rh(P_4S_3)]CF_3SO_3$ [E = N (**5**), P (**6**)] indicate, at variance with the spectra of the P_4Se_3 derivatives, the presence of two species, whose ratio depends on the ligand: the most abundant compound is ≈90% for **5** and ≈80% for **6**. These data are interpreted as due to the existence of a pair of coordination isomers which differ for the bonding mode of the P_4S_3 molecule to the metal fragment, i.e. through the apical P or through one of the basal P atoms (Scheme 2). The ^{31}P,^{31}P COSY NMR spectra of **5** and **6**, showing two sets of correlated peaks, support such interpretation. The major isomer of **6** exhibits a first order A_3CFM_3Z spin system (Table 1) and its spectral features parallel those of the P_4Se_3 derivative **4**; they are accordingly indicative of a trigonal bipyramidal coordination around the metal with the apical phosphorus of the intact cage occupying the axial position *trans* to the apical phosphorus of the PP_3 ligand.

The minor isomer exhibits an A_3CFM_2QZ spin system (Table 1) which is consistent with a trigonal bipyramidal geometry around the metal and the P_4S_3 cage molecule being bound to the metal through one of the basal phosphorus atoms. The signals of the tripodal PP_3 ligand show minor deviations with respect to those observed in the major isomer and in **4**. The four phosphorus atoms of the heptatomic cage form the FM_2Q part of the spin system (Table 1). The two equivalent uncoordinated basal P_M atoms yield a broad doublet of doublets characterized by a large one-bond coupling (230.0 Hz, Table 1) to P_Q and a small one with P_F. Inspection of Table 1 shows also that P_Q exhibits a notable downfield shift with respect to the three equivalent P atoms of the free cage, whereas P_M is only moderately

Table 1
$^{31}P\{^{1}H\}$ NMR data of the free and coordinated P_4Se_3 and P_4S_3 ligands[a]

Compound	Chemical shift, δ (ppm)			Coupling constant, J(Hz)			
	P_F	P_M	P_Q	$^{2}J(P_F–P_M)$	$^{2}J(P_F–P_Q)$	$^{1}J(P_M–P_Q)$	
P_4Se_3	30.7 (q)	−114.1 (d)		72.0			
3 E = N[b]	102.8 (m)	−104.3 (d)		26.5			
4 E = P[b]	106.2 (m)	−102.3 (d)		29.3			
P_4S_3	65.1 (q)	−127.3 (d)		70.0			
5 E = N[b] major isomer	140.2 (dm)	−110.2 (d)		22.0			$^{1}J(P_F$-Rh) 131.0
5 minor isomer	97.1 (dt)	−140.8 (dd)	14.7 (m)	65.5	43.5	238.5	$^{1}J(P_Q$-Rh) 130.0
6 E = P[c] major isomer	136.4 (m)	−109.6 (d)		28.0			
6 minor isomer	88.9 (dt)	−139.6 (ddm)	11.7 (m)	64.5	46.0	230.0	
7[b]	144.9 (dm)	−116.6 (dm)	14.5 (m)			205.5	$^{1}J(P_F$-Rh) 119.0

[a] The NMR spectra were recorded at room temperature (20 °C) with a Varian Gemini g300bb spectrometer. Key: d = doublet, t = triplet, q = quartet, m = multiplet.
[b] Spectrum recorded in CD_2Cl_2.
[c] Spectrum recorded in $(CD_3)_2CO$.

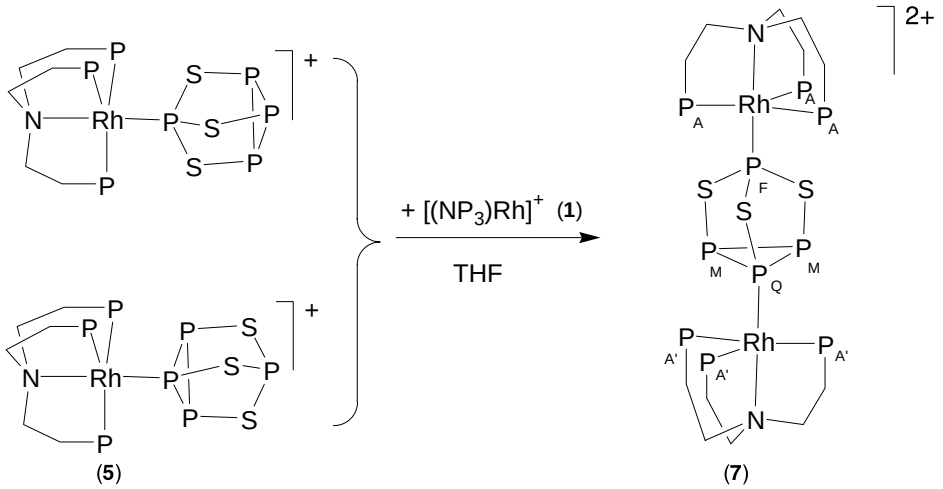
shielded. The uncoordinated P_F atom appears as a doublet of triplets which is slightly downfield shifted with respect to the free molecule.

The $^{31}P\{^{1}H\}$ NMR spectra of **5** have been run at different temperatures (from −80 to +40 °C) and, remarkably, the relative amount of the two isomers does not change, ruling out any exchange process between the two species. The signals due to the major isomer do not change in the range of the investigated temperatures, while those of the minor isomer start broadening below −10 °C, but do not resolve even at the lowest reached temperature. Anyhow, the inequivalence of the two basal uncoordinated phosphorus atoms is suggested by the broad doubling of their resonance. The reversibility of this process points to the presence of a dynamic behaviour which should feature a low activation barrier suggesting limited changes in the stereochemistry of the coordinated cage.

The results obtained from the NMR analysis of isolated samples of **3** and **5**, have been combined by ^{31}P NMR studies on the reaction of **1** and P_4X_3 in solution. In fact, the *ortho*-metallated hydride **1**, Scheme 2, exhibits an AMQZ $^{31}P\{^{1}H\}$ NMR spectrum with the P_Q atom, involved in a four-membered metallo ring, at high field (−34.08 ppm), well apart from the other phosphorus atoms of NP_3. Such feature is a valuable probe to follow the reaction of **1**, which easily restores the 16-electron fragment $[(NP_3)Rh]^+$ by addition of suitable substrates [16]. In the case at hand, the fast disappearance of the high field P_Q signal in the reaction of **1** with P_4S_3 suggests that the reaction completes to yield the two isomers in a ratio similar to that observed by dissolving **5**. In contrast, $^{31}P\{^{1}H\}$ NMR analysis of the reaction of **1** at room temperature with P_4Se_3 provides evidence only for the apical isomer and, interestingly, some *ortho*-metallated species remains always unreacted. These results suggest that the P_4Se_3 molecule is a weaker donor with respect to P_4S_3.

The monometal species $[(NP_3)Rh(\eta^1\text{-}P_4S_3)]CF_3SO_3$ (**5**) dissolved in THF reacts with **1** to form (Scheme 3), after workup, the dimetal compound $[\{(NP_3)Rh\}_2(\mu, \eta^{1:1}\text{-}P_{apical},\text{-}P_{basal}\text{-}P_4S_3)](CF_3SO_3)_2$ (**7**). The ^{31}P NMR spectrum of the compound (Table 1) yields an $A_3A_3'FM_2QZZ'$ spin system, consistent with double metallation of the P_4S_3 molecule, which holds the two non-equivalent $[\{(NP_3)Rh\}]^+$ metal units together and is responsible for the FM_2Q part of the spin system. The apical and the basal phosphorus atoms of P_4S_3 bound to the metals undergo a significant downfield shift upon coordination; the same trend, although less pronounced, has been observed for the $[\{(triphos)Re(CO)_2\}_2(\mu, \eta^{1:1}\text{-}P_{apical},\text{-}P_{basal}\text{-}P_4Se_3)]^{2+}$ cation [14]. Although polymetallic cluster compounds containing two [9] or three [10] bridging P_4S_3 units, formed through activation of a P–P bond, and tetrametallic compounds containing the P_4Se_3 unit, resulting from the cleavage of P–P and P–Se bonds, [8] have been described, the present dimetal species exhibits the intact P_4S_3 molecule in bridging position between two transition metal fragments, in analogy with the recently reported P_4S_3 silver adducts [15].

The $[(NP_3)Rh]^+$ and the $[(PP_3)Rh]^+$ fragments are known to promote the activation of C–H, H–H, [16] S–H [17] bonds and, significant for the present work, the $[(NP_3)Rh]^+$ moiety may also induce one P–P breaking of the P_4 molecule [18]. Notwithstanding, no insertion of the metal fragment into a P–P or P–X bond of the cage occurs in the complexes here reported. This study, in connection with the results described for rhenium complexes with P_4X_3, [14] provides experimental evidence that both types of phosphorus atoms in the P_4X_3 cage have comparable coordinating properties and that subtle geometric and electronic effects due to the metal-ligand fragments determine whether the apical or the basal donor is preferred for coordination. The P–X or P–P activation of the sterically demanding P_4X_3 cage



Scheme 3.

should involve a trigonal pyramidal → pseudooctahedral rearrangement of the metal fragment with an excessive opening of one of the P–Rh–P angles formed by peripheral P atoms of the tripodal ligand [20].

3. Experimental section

3.1. General

All reactions and manipulations were performed under an atmosphere of dry oxygen-free argon. THF and toluene were freshly distilled from sodium. The $^{31}P\{^1H\}$ NMR spectra were measured on a Varian Gemini g300bb spectrometer, equipped with a variable-temperature unit, operating at 121.46 MHz. Chemical shifts are relative to H_3PO_4 85% as external standards at 0.00 ppm. Analytical data for carbon and hydrogen were obtained from the Microanalytical Laboratory of the Department of Chemistry of the University of Firenze. The hydride complexes [(NP_3)RhH] and [(PP_3)RhH] were prepared according to the literature methods [16]. P_4S_3 was purchased from Fluka AG and recrystallized from toluene prior the use; P_4Se_3 was prepared by melting red phosphorus and grey selenium as described in the literature [21]. CF_3SO_3Me (Aldrich) was used as purchased and stored at 0 °C. The $^{31}P\{^1H\}$ NMR data of the tripodal ligands in the compounds are reported in this section. The uninformative ^1H and $^{13}C\{^1H\}$ signals of the ligands are not reported.

3.2. Syntheses

3.2.1. [(NP_3) Rh(P_4Se_3)]CF_3SO_3, (**3**)

Neat CF_3SO_3Me (0.30 mmol) was added at room temperature to [(NP_3)RhH] (204 mg, 0.27 mmol) dissolved in THF (30 cm^3). The solution was stirred for 20 min and then added to P_4Se_3 (97 mg, 0.27 mmol) dissolved in toluene (30 cm^3). The resulting solution was stirred for 2 h while turning dark red; it was concentrated to ≈35 cm^3 at reduced pressure and then cooled to −20 °C. Brown crystals separated within seven days. The solid was collected by filtration, washed with toluene, petroleum ether and dried. Yield 55%. $C_{43}H_{42}F_3NO_3P_7RhSSe_3$ (1266.4). Calc.: C, 40.8; H, 3.34; N, 1.10. Found: C, 40.6; H, 3.30; N, 1.06%. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 298 K): 33.8 (3P, P_A, dd, $^1J(P_A\text{-Rh})$ 122.5, $^2J(P_A–P_F)$ 16.5).

3.2.2. [(PP_3)Rh(P_4Se_3)]CF_3SO_3(**4**)

The compound was prepared through the procedure described for **3** by adding CF_3SO_3Me to [(PP_3)RhH]. Yield 50%. $C_{43}H_{42}F_3O_3P_8RhSSe_3$ (1283.4). Calc.: C, 40.2; H, 3.30; P, 19.3. Found: C, 39.8; H, 3.20; P, 19.0%. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 298 K): δ 156.4 (1P, P_C, ddq, $^1J(P_C\text{-Rh})$ 127.0, $^2J(P_C–P_A)$ 20.0, $^2J(P_C–P_F)$ 36.0), 53.4 (3P, P_A, ddd, $^1J(P_A\text{-Rh})$ 131.5, $^2J(P_A–P_F)$ 17.0).

3.2.3. [(NP_3)Rh(P_4S_3)]CF_3SO_3,(**5**)

1 (0.3 mmol), prepared as described for the synthesis of **3**, was added at room temperature to the stoichiometric amount of P_4S_3 in THF (25 cm^3). Toluene (10 cm^3) was added and the resulting dark brown solution was concentrated at reduced pressure and cooled to −20 °C. The dark red crystals which separated within seven days were collected, washed with toluene, petroleum ether and dried.

Yield 85%. $C_{43}H_{42}F_3NO_3P_7RhS_4$ (1125.7). Calc.: C, 45.9; H, 3.76; N, 1.24; P, 19.3. Found: C, 45.4; H, 3.54; N, 1.20; P, 19.2%. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 298 K); major isomer: δ 32.4 (3P, P_A, dd, $^1J(P_A\text{-Rh})$ 134.5,

$^2J(P_A–P_F)$ 35.5). Minor isomer: 33.8 (3P, P_A, dd, $^1J(P_A$-Rh) 135.0, $^2J(P_A–P_Q)$ 35.5).

3.2.4. [(PP$_3$)Rh(P$_4$S$_3$)]CF$_3$SO$_3$, (6)

Complex **6** was prepared as described above for **5** by using **2** (0.3 mmol) in place of **1**. Yield 80%. $C_{43}H_{42}F_3O_3P_8RhS_4$ (1142.7). Calc.: C, 45.2; H, 3.70; S, 11.2. Found: C, 44.5; H, 3.62; S, 10.5%. $^{31}P\{^1H\}$NMR ($(CD_3)_2CO$, 298 K); maior isomer: δ 158.6 (1P, P_C, ddq, $^1J(P_C$-Rh) 120.5, $^2J(P_C–P_A)$ 22.0, $^2J(P_C–P_F)$ 32.5), 52.7 (3P, P_A, ddd, $^1J(P_A$-Rh) 133.0, $^2J(P_A–P_F)$ 36.0). Minor isomer: 161.8 (1P, P_C, ddq, $^1J(P_C$-Rh) 102.5, $^2J(P_C–P_A)$ 21.0, $^2J(P_C–P_Q)$ 39.0), 51.0 (3P, P_A, ddd, $^1J(P_A$-Rh) 132.5, $^2J(P_A–P_Q)$ 41.0).

3.2.5. [{(NP$_3$)Rh}$_2$(P$_4$S$_3$)](CF$_3$SO$_3$)$_2$(7)

The $[(NP_3)Rh]^+$ fragment (1) (0.25 mmol), prepared as described for the synthesis of (**3**), was added at room temperature to a solution of **3** (250 mg; 0.22 mmol) in THF (20 cm^3). The resulting solution was stirred for 2 h and toluene (15 cm^3) was added. Brown microcrystals were obtained by slowly evaporating the resulting solution. The solid was filtered out and washed with toluene and light petroleun before being dried. Yield 60%. $C_{86}H_{84}F_6N_2O_6P_{10}Rh_2S_5$ (2031.3). Calc.: C, 50.8; H, 4.17; N, 1.38; S, 7.89. Found: C, 50.2; H, 4.07; N, 1.28; S, 7.50%. $^{31}P\{^1H\}$NMR (CD_2Cl_2, 298 K): δ 34.1 (3P, P_A, dd, $^1J(P_A$-Rh) 134.0, $^2J(P_A–P_F)$ 35.0), 33.7 (3P, $P_{A'}$, dd, $^1J(P_{A'}$-Rh) 135.5, $^2J(P_{A'}–P_Q)$ 37.5).

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