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Rhodium(I) complexes with κ*P* coordinated ω-phosphinofunctionalized alkyl phenyl sulfide, sulfoxide and sulfone ligands and their reactions with sodium bis(trimethylsilyl)amide and Ag[BF_4]

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ABSTRACT

Reactions of ω-diphenylphosphinofunctionalized alkyl phenyl sulfides $Ph_2P(CH_2)_nSPh$ ($n = 1$, **1a**; 2, **2a**; 3, **3a**), sulfoxides $Ph_2P(CH_2)_nS(O)Ph$ ($n = 1$, **1b**; 2, **2b**; 3, **3b**) and sulfones $Ph_2P(CH_2)_nS(O)_2Ph$ ($n = 1$, **1c**; 2, **2c**; 3, **3c**) with dinuclear chlorido bridged rhodium(I) complexes $[(RhL_2)_2(\mu\text{-}Cl)_2]$ (L_2 = cycloocta-1.5-diene, cod, **4**; bis(diphenylphosphino)ethane, dppe, **5**) afforded mononuclear Rh(I) complexes of the type [RhCl{$Ph_2P(CH_2)_nS(O)_x$Ph-κ*P*}(cod)][1] ($n/x = 1/0$, **6a**; 1/1, **6b**; 1/2, **6c**; 2/0, **8a**; 2/1, **8b**; 2/2, **8c**; 3/0, **10a**; 3/1, **10b**; 3/2, **10c**) and [RhCl{$Ph_2P(CH_2)_nS(O)_x$Ph-κ*P*}(dppe)] ($n/x = 1/0$, **7a**; 1/1, **7b**; 1/2, **7c**; 2/0, **9a**; 2/1, **9b**; 2/2, **9c**; 3/0, **11a**; 3/1, **11b**; 3/2, **11c**) having the P^S(O)$_x$ ligands κ*P* coordinated. Addition of Ag[BF_4] to complexes **6**–**11** in CH_2Cl_2 led with precipitation of AgCl to cationic rhodium complexes of the type [Rh{$Ph_2P(CH_2)_nS(O)_x$Ph-κ*P*,κ*S*/*O*}L_2][BF_4] having bound the P^S(O)$_x$ ligands bidentately in a κ*P*,κ*S* (**13a**–**18a**, **15b**–**18b**) or a κ*P*,κ*O* (**13b**, **14b**, **13c**–**18c**) coordination mode. Unexpectedly, the addition of Ag[BF_4] to **6a** in THF afforded the trinuclear cationic rhodium(I) complex $[Rh_3(\mu\text{-}Cl)(\mu\text{-}Ph_2PCH_2SPh\text{-}\kappa P{:}\kappa S)_4][BF_4]_2 \cdot 4THF$ (**12**·4THF) with a four-membered Rh_3Cl ring as basic framework. Addition of sodium bis(trimethylsilyl)amide to complexes **6**–**11** led to a selective deprotonation of the carbon atom neighbored to the S(O)$_x$ group (α-C) yielding three different types of organorhodium complexes: a) Organorhodium intramolecular coordination compounds of the type [Rh{CH{S(O)$_x$Ph}$CH_2CH_2PPh_2$-κ*C*,κ*P*}L_2] (**22a**–**c**, **23a**–**c**), b) zwitterionic complexes [Rh{$Ph_2PCHS(O)_x$Ph-κ*P*,κ*S*/*O*}L_2] having κ*P*,κ*S* (**21a**, **21b**) and κ*P*,κ*O* (**20b**/**c**, **21c**) coordinated anionic [$Ph_2PCHS(O)_x$Ph] ligands, and c) the dinuclear rhodium(I) complex [{Rh{μ-CH(SPh)PPh_2-κ*C*:κ*P*}(cod)}$_2$] (**19**). All complexes were fully characterized spectroscopically and complexes **15b**, **15c**, **12**·4THF and **19**·THF additionally by X-ray diffraction analysis. DFT calculations of zwitterionic complexes gave insight into the coordination mode of the [Ph_2PCHS(O)Ph] ligand (κ*P*,κ*S* versus κ*P*,κ*O*).

1. Introduction

Sterical and electronical effects of bidentate ligands on the structure and reactivity of metal complexes are a substantial subject of research in organometallic chemistry as well as in homogeneous catalysis. While many investigations were done with homobidentate ligands such as diphosphanes [1–3], heterobidentate ligands offer the possibility to introduce two completely different donor centers having different electronic (e.g. trans influence, trans effect) and sterical effects. In this way, stability and reactivity of intermediates in a reaction may be influenced in a targetted manner [4,5]. As an example, bidentate P^S and P^O type ligands are equipped with a strong and a weak donor group; thus, they might offer a hemilabile character which permits a temporary generation of a vacant coordination site at the metal center [6]. Moreover, complexes bearing ligands of that type can play an important role in various homogeneously catalyzed reactions [7–10] or as chemosensors [11].

Furthermore, deprotonation of such ligands may lead to the formation of zwitterionic (betaine-like) complexes. They are characterized by a formal charge separation between a cationic metal center and a negatively charged ancillary ligand moiety within an overall neutral molecular framework [12]. Hence, they combine the reactivity of related cationic complexes with the solubility properties of neutral species which makes them useful in some homogeneously catalyzed reactions [13–15]. If the deprotonation of the P^S and P^O ligands leads to a κ*C*,κ*P* coordination, organometallic intramolecular coordination compounds (also named "organometallic inner complexes")

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[1] Here and in the following the letters **a**, **b**, and **c** in the numbering schemes refer to a sulfanyl ($x = 0$), sulfinyl ($x = 1$) and sulfonyl ($x = 2$) functionality, respectively.

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are formed. In general, they are characterized as metallacyclic compounds with an M–C bond and a bond of the metal to a neutral Lewis-basic heteroatom group like NR_2, PR_2, OR or SR being also part of the cycle. Over the past years, they were subject of a large number of researches [16–19], thus, from almost all metals of the periodic table organometallic intramolecular coordination compounds are known and they are widely used in various ways in organic syntheses.

We are interested in α,ω-functionalized ligands of the type $R_mY(CH_2)_nS(O)_xR$ bearing a Lewis-basic heteroatom group YR_m (YR_m = PR_2, NR_2, OR; R = alkyl, aryl) as well as, respectively, a sulfanyl ($x = 0$), sulfinyl ($x = 1$) and sulfonyl group ($x = 2$). While the functionalized sulfides and sulfones can act as κ*S*,κ*Y* and κ*O*,κ*Y* donors, respectively, in case of the analogous flexidentate sulfoxides both coordination modes are possible [20–22]. Structure and reactivity of metal complexes with the requisite deprotonated ligands depend on the nature of sulfur functionalization neighbored to the carbanionic atom (α-C). Ligands with a Lewis-basic sulfide group ($x = 0$) next to the α-carbon atom are found to be κ*C*,κ*Y* coordinated in most cases, thereby organometallic intramolecular coordination compounds are formed, irrespective of the nature of the metal [23–26]. However, in the analogous complexes with a functionalized sulfone ligand ($x = 2$) the dipole stabilization of the SO_2 group gives rise to the formation of a less basic carbanion [27]. While in solid state the majority of the respective lithiated compounds are higher aggregated having the sulfonyl group κ*O* coordinated to the Li atom resulting in a "free" carbanionic center [28] the corresponding transition metal complexes were generally found to be mononuclear organometallic intramolecular coordination compounds exhibiting a κ*C*,κ*Y* coordination [29,30]. On the other hand, the sulfinyl functionalization ($x = 1$) can be regarded both as a Lewis-basic and a dipole-stabilized heteroatom group. Yet there have been only few studies on these ligands; even for non-functionalized ligands of the type $^{\ominus}$CHR–S(O)R only few structural data are presented in the literature. They seem to resemble more the sulfones: lithiated sulfoxides exhibit a κ*O* coordination with a "free" carbanionic center [31] whereas in transition metal complexes a κ*C* coordination is observed [32].

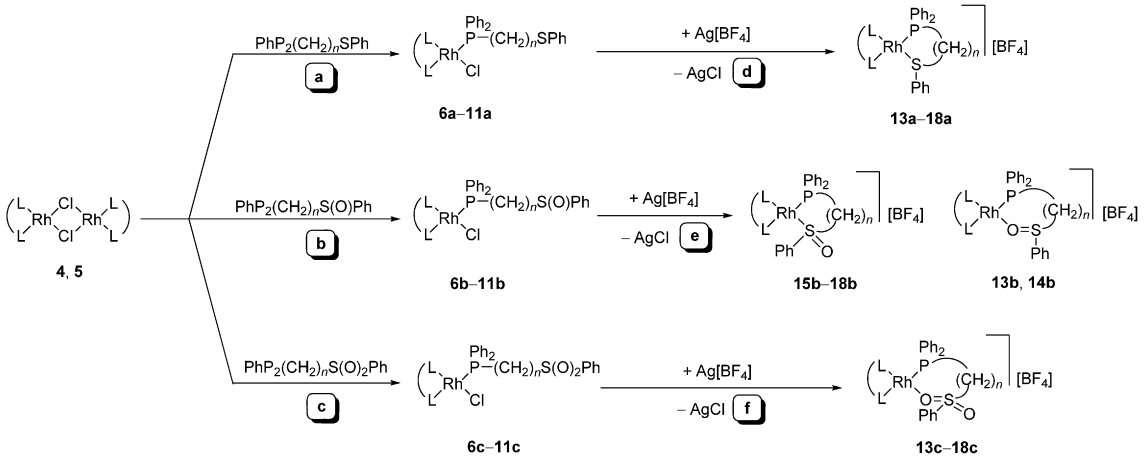
Here we present a systematic study on reactions of rhodium(I) complexes of the type $[RhCl\{Ph_2P(CH_2)_nS(O)_xPh\text{-}\kappa P\}L_2]$ (L_2 = cod, dppe) with sodium bis(trimethylsilyl)amide and $Ag[BF_4]$, respectively, in dependence on the type of the sulfur functionalization ($x = 0$–2) and on the spacer length (n = 1–3). Thus, it is reported on the formation and characterization of organorhodium intramolecular coordination compounds and zwitterionic complexes having the deprotonated P^S(O)$_x$ ligands κ*C*,κ*P*, κ*P*,κ*S* and κ*P*,κ*O* coordinated as well as of cationic complexes with non-deprotonated P^S(O)$_x$-κ*P*,κ*S*/*O* ligands.

2. Results and discussion

2.1. Syntheses

Chlorido bridged Rh(I) complexes $[(RhL_2)_2(\mu\text{-}Cl)_2]$ (L_2 = cod, **4**; dppe, **5**) were reacted with compounds of the type $Ph_2P(CH_2)_nS(O)_xPh$ that include ω-diphenylphosphinofunctionalized alkyl phenyl sulfides ($x = 0$), sulfoxides ($x = 1$) and sulfones ($x = 2$). As spacers between the two donor sites the methylene ($n = 1$), dimethylene ($n = 2$) and trimethylene ($n = 3$) groups were used. As shown in Scheme 1 (routes **a**/**b**/**c**) the reactions afforded neutral rhodium(I) complexes (**6a**/**b**/**c**–**11a**/**b**/**c**) having bound the $Ph_2P(CH_2)_nS(O)_xPh$ ligands in a κ*P* coordination mode as it was shown for complexes **10a**/**11a** [24] and **10c**/**11c** [29] before. The reactions were conducted in THF at room temperature. Using methylene chloride as solvent, the reactions with the dppe complex **5** have to be performed at −78 °C to avoid the oxidative addition of methylene chloride to **5** which results in the formation of a methylene-bridged rhodium(III) complex [33]. Complexes **6**–**11** were obtained as yellow to orange moderately air and moisture sensitive solids in good to excellent yields (72–91%) and they were characterized NMR spectroscopically (^1H, ^{13}C, ^{31}P) as well as by high-resolution mass spectrometric (HRMS-ESI) investigations. All complexes were soluble in THF and CH_2Cl_2. Solutions were found to be stable at room temperature, except for complexes **8a** and **8b** that showed a decomposition within several hours. In chloroform all complexes (except of **6**, **8c** and **10**) decomposed within several minutes.

Addition of $Ag[BF_4]$ to complexes **6a**/**b**/**c**–**11a**/**b**/**c** led with precipitation of AgCl to cationic rhodium complexes of the type $[Rh\{Ph_2P(CH_2)_nS(O)_xPh\text{-}\kappa P,\kappa S/O\}L_2][BF_4]$ (**13a**/**b**/**c**–**18a**/**b**/**c**) bearing chelating P^S(O)$_x$ ligands with a κ*P*,κ*S* and a κ*P*,κ*O* coordination mode, respectively (Scheme 1, routes **d**/**e**/**f**). To simplify these



	4	5	6	7	8	9	10	11	13	14	15	16	17	18
n	–	–	1	1	2	2	3	3	1	1	2	2	3	3
L L	cod	dppe	cod	dppe	cod	dppe	cod	dppe	cod	dppe	cod	dppe	cod	dppe

Scheme 1. Synthesis of rhodium complexes bearing monodentately coordinated P^S(O)$_x$-κ*P* ligands (**6**–**11**) and chelating P^S(O)$_x$-κ*P*,κ*S*/*O* ligands (**13**–**18**).

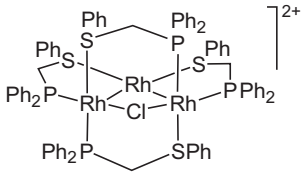


Chart 1. Structural formula of the cation in $[Rh_3(\mu\text{-}Cl)(\mu\text{-}Ph_2PCH_2SPh\text{-}\kappa P{:}\kappa S)_4][BF_4]_2\cdot 4THF$ (**12**·4THF).

syntheses, the neutral complexes **6**–**11** obtained via routes **a**/**b**/**c** do not have to be isolated. In such a way complexes **13**–**18** were isolated in yields of 78–92% as yellow moderate air and moisture sensitive solids. While **16c** showed only a limited stability in CH_2Cl_2 (ca 1 h at room temperature) all other complexes were soluble in methylene chloride without decomposition.

Complexes **13**–**18** were characterized by ^1H, ^{13}C, ^{31}P NMR spectroscopy as well as by HRMS-ESI measurements. The phosphinofunctionalized sulfides ($x = 0$) and sulfones ($x = 2$) are $\kappa P,\kappa S$ and $\kappa P,\kappa O$ coordinated, respectively. The corresponding sulfoxides exhibit both a $\kappa P,\kappa S$ ($n = 2, 3$) and a $\kappa P,\kappa O$ ($n = 1$) coordination, thus forming five- and six-membered rhodacycles. ^{31}P NMR spectroscopic measurements of the reaction solutions showed that all reactions were highly selective with the exception of complex **18c** where several by-products (>60%) were found which could not be removed. Furthermore, attempts failed to obtain complex **18c** alternatively by ligand substitution (cod → dppe) from complex **17c**: As shown NMR spectroscopically, adding 1 equivalent dppe to complex **17c** resulted with cleavage of cod in the formation of the two homoleptic cationic complexes $[Rh(dppe)_2]^+$ and $[Rh\{Ph_2PCH_2CH_2CH_2S(O)_2Ph\text{-}\kappa P,\kappa O\}_2]^+$.

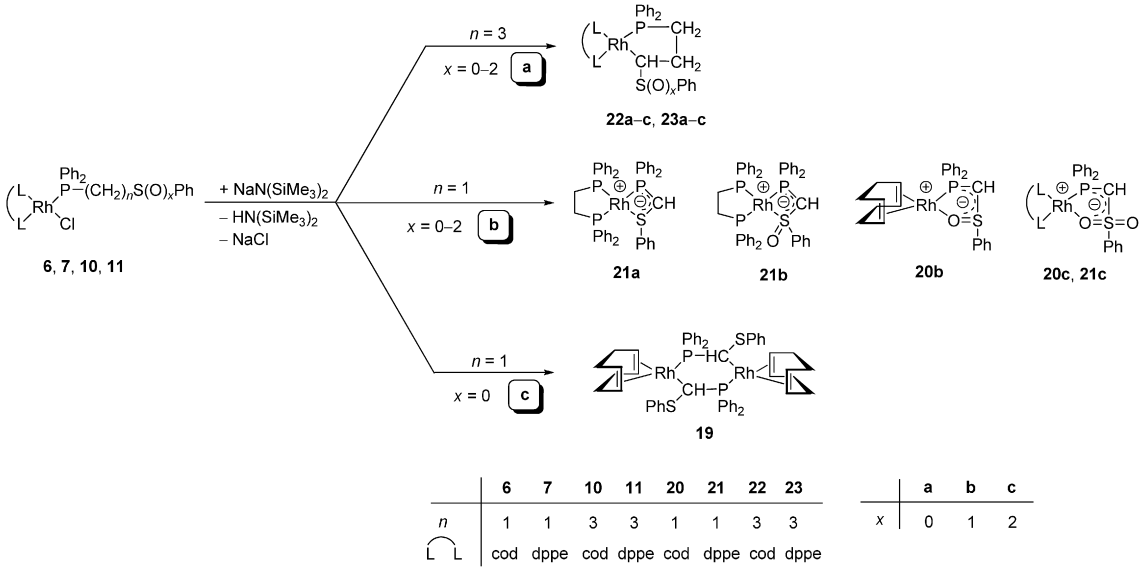
While the addition of $Ag[BF_4]$ to complex **6a** in CH_2Cl_2 afforded selectively the cationic rhodium complex **13a** (Scheme 1), the analogous reaction performed in THF led to the immediate formation of a deep red solution which contains three different complexes in a ratio of about 2:1:2 as revealed by ^{31}P NMR spectroscopic measurements. Within 24 h, one of these products precipitated as red crystals which were isolated in a yield of 32%. NMR spectroscopic and structural measurements exhibited that a trinuclear rhodium(I) complex, $[Rh_3(\mu\text{-}Cl)(\mu\text{-}Ph_2PCH_2SPh\text{-}\kappa P{:}\kappa S)_4][BF_4]_2\cdot 4THF$ (**12**·4THF; Chart 1), has been formed.

Reactions of the neutral rhodium complexes **6**–**11** with sodium bis(trimethylsilyl)amide at −78 °C led to a selective deprotonation of the α-carbon atom yielding three different types of organorhodium complexes (Scheme 2, routes **a**/**b**/**c**):

*Route **a***. Starting from the neutral complexes having a trimethylene spacer ($n = 3$; **10**, **11**) organorhodium intramolecular coordination compounds of the type $[Rh\{CH\{S(O)_xPh\}CH_2CH_2PPh_2\text{-}\kappa C,\kappa P\}L_2]$ (**22**, **23**) were obtained. The two complexes bearing the deprotonated sulfinylfunctionalized ligand ($x = 1$; **22b**, **23b**) were isolated in yields of about 75% as yellow highly air and moisture sensitive solids which were found to be soluble in THF and CH_2Cl_2 without decomposition. Moreover, they showed a moderate solubility in *n*-pentane. Complexes **22a**/**c** and **23a**/**c** have been prepared before by using lithium diisopropyl amide as base [24,29]. Hence, in this work the formation of these complexes has been proved by ^{31}P NMR spectroscopic measurements of the reaction solutions only.

*Route **b***. The second class are zwitterionic complexes of the type $[Rh\{Ph_2PCHS(O)_xPh\text{-}\kappa P,\kappa S/O\}L_2]$ (**20**, **21**) which were obtained by starting from the neutral complexes bearing a methylene spacer ($n = 1$; **6**, **7**). These complexes have $\kappa P,\kappa S$ (**21a**, **21b**) and $\kappa P,\kappa O$ (**20b**/**c**, **21c**) coordinated anionic $[Ph_2PCHS(O)_xPh]$ ligands, thus the methine C atom is not coordinated to Rh. The complexes were obtained as brown highly air and moisture sensitive solids showing limited thermal stability only. Due to that, they were isolated without removing the NaCl formed in the course of the reaction. Furthermore, they exhibited a pronounced solubility even in *n*-pentane which made it difficult to remove residual amounts of $HN(SiMe_3)_2$. Complex **21a** was characterized by ^{31}P NMR spectroscopy from the reaction mixture only. All attempts to isolate complex **21a** in substance led to decomposition. Complexes **20c** and **21b** were found to decompose in THF within 1 h at room temperature and immediately in methylene chloride. For complexes **20b** and **21c** the opposite was the case. Complexes **20**–**23** (except of complex **21a**) were characterized by NMR spectroscopy (^1H, ^{13}C, ^{31}P) and HRMS-ESI measurements.

*Route **c***. In contrast, the reaction of the neutral complex [RhCl(Ph_2PCH_2SPh-κ*P*)(cod)] (**6a**) with $NaN(SiMe_3)_2$ led to the formation of the dinuclear rhodium complex $[\{Rh\{\mu\text{-}CH(SPh)PPh_2\text{-}\kappa C{:}\kappa P\}(cod)\}_2]$ (**19**). As ^{31}P NMR spectroscopic measurements from the reaction mixture revealed, the reaction proceeded with a high selectivity (>90%), too. Within 24 h, **19** crystallized from the reaction mixture as THF adduct (**19**·THF) in a yield of 81% as orange



Scheme 2. Synthesis of organorhodium intramolecular coordination compounds (**22**, **23**), zwitterionic complexes (**20**, **21**) and a dinuclear organorhodium complex (**19**).

Table 1
Selected NMR spectroscopic data (δ in ppm, J in Hz) of [RhCl{$Ph_2P(CH_2)_nS(O)_xPh$-κ*P*}L_2] (**6**–**11**).

L (x)	$Ph_2PC_\alpha H_2S(O)_xPh$			$Ph_2PC_\beta H_2C_\alpha H_2S(O)_xPh$				$Ph_2PC_\gamma H_2CH_2C_\alpha H_2S(O)_xPh$			
		$\delta_{\alpha\text{-C}}$ ($^1J_{P,C}$)	δ_P ($^1J_{Rh,P}$)		$\delta_{\alpha\text{-C}}$ ($^2J_{P,C}$)	$\delta_{\beta\text{-C}}$ ($^1J_{P,C}$)	δ_P ($^1J_{Rh,P}$)		$\delta_{\alpha\text{-C}}$ ($^3J_{P,C}$)	$\delta_{\gamma\text{-C}}$ ($^1J_{P,C}$)	δ_P ($^1J_{Rh,P}$)
cod (0)	**6a**	31.4 (17.8)	28.1 (150.1)	**8a**	36.9 (7.2)	31.4 (15.9)	26.1 (150.7)	**10a**[a]	35.4 (15.0)	26.9 (25.2)	26.2 (147.1)
cod (1)	**6b**	62.3 (18.3)	30.8 (151.2)	**8b**	52.9 (s)	20.1 (22.9)	26.8 (151.2)	**10b**	58.0 (12.1)	26.9 (25.3)	26.8 (146.4)
cod (2)	**6c**	54.9 (6.8)	24.0 (154.1)	**8c**	53.5 (2.7)	22.6 (23.6)	24.7 (153.2)	**10c**[b]	57.1 (13.8)	26.6 (25.2)	27.8 (149.2)
dppe (0)	**7a**	32.0 (13.7)	24.4 (132.2)	**9a**	38.4 (9.0)	32.4 (22.8)	60.6 (134.9)	**11a**[a]	35.4 (15.8)	28.4 (22.7)	23.8 (131.6)
dppe (1)	**7b**	63.1 (13.8)	27.9 (142.3)	**9b**	53.6 (6.3)	20.4 (21.6)	23.1 (133.2)	**11b**	58.7 (13.0)	27.1 (21.9)	24.2 (131.5)
dppe (2)	**7c**	53.7 (6.9)	22.0 (135.0)	**9c**	52.7 (5.1)	21.2 (19.6)	22.1 (133.8)	**11c**[b]	57.6 (13.6)	26.9 (22.5)	23.7 (131.6)

[a] Values taken from Ref. [24].
[b] Values taken from Ref. [29].

moderately air and moisture sensitive crystals being suitable for a single-crystal X-ray diffraction analysis. Moreover, the isolated product was found to be insoluble in all common solvents which prevented further NMR spectroscopic characterization.

By analogy to the synthesis of the cationic rhodium complexes **13**–**18**, for the synthesis of all these complexes (**19**–**23**) the intermediate compounds **6**–**11** do not have to be isolated. Hence, complexes **19**–**23** can be obtained in a one-pot procedure directly from the dinuclear starting complexes **4** and **5**. In no case we succeeded to obtain definite complexes starting from rhodium complexes bearing P^S(O)$_x$ ligands with the dimethylene spacer ($n = 2$; **8**, **9**) since all reactions with $NaN(SiMe_3)_2$ led to decomposition, as ^{31}P NMR spectroscopic investigations revealed.

2.2. Spectroscopic investigations

2.2.1. Rhodium complexes with $Ph_2P(CH_2)_nS(O)_xPh$-κ*P* ligands (n = 1–3, x = 0–2)

Selected NMR spectroscopic parameters of complexes **6**–**11** are given in Table 1. The ^{31}P NMR spectra were of first order where all dppe complexes (**7**, **9**, **11**) exhibited an AEMX spin system and all cod complexes (**6**, **8**, **10**) an AX spin system (A, E, M = ^{31}P; X = ^{103}Rh). The κ*P* coordination of the P^S(O)$_x$ ligands went along with a strong lowfield shift of the ^{31}P resonances ($\Delta\delta_P > 30$ ppm). The $^1J_{P,C}$ couplings for ligands with the same spacer length (**6**/**7**, **8**/**9**, **10**/**11**) were in a narrow range, with the exception of **6c**, **7c** and **8c**. In all dppe complexes (**7**, **9**, **11**) the $^1J_{Rh,P}$ couplings (P is part of the P^S(O)$_x$ ligands) were about 20 Hz smaller than those of the cod complexes (**6**, **8**, **10**) reflecting the higher trans influence of phosphanes compared to olefines [34]. Due to the chiral sulfur center in the rhodium complexes bearing ω-phosphinofunctionalized alkyl phenyl sulfoxide ligands (**6b**–**11b**) the aliphatic and olefinic (**6b**, **8b**, **10b**) hydrogen atoms are diastereotopic. The best it could be seen in case of complexes **6b** and **7b** where each of the aliphatic protons of the $Ph_2PCH_2S(O)Ph$-κ*P* ligand exhibited a doublet of doublet pattern caused by $^2J_{H,H}$ (13.5/13.5 Hz, **6b**; 13.3/13.3 Hz, **7b**) and $^2J_{P,H}$ couplings (9.1/8.0 Hz, **6b**; 7.4/6.4 Hz, **7b**). Due to signal overlapping and/or additional H,H couplings only broad signals or non-resolved multiplets were observed in the other complexes bearing ligands with a sulfinyl functionalization.

2.2.2. Cationic rhodium complexes bearing P,S and P,O chelate ligands and $[Rh_3(\mu\text{-}Cl)(\mu\text{-}Ph_2PCH_2SPh\text{-}\kappa P{:}\kappa S)_4][BF_4]_2\cdot 4THF$

Selected NMR spectroscopic parameters of complexes **13**–**18** are given in Table 2. The ^{31}P NMR spectra of the complexes bearing a dppe ligand appeared as first order AEMX spin systems (**14a**, **14c**, **16c**, **18a**, **18b**, **18c**) as well as higher order ABMX (**14b**, **16a**) and ABCX (**16b**) spin systems, respectively (A, B, C, E, M = ^{31}P; X = ^{103}Rh) which were analyzed by using the PERCH NMR software package [35]. The ^{31}P NMR spectra of all cod complexes (**13**, **15**, **17**) were AX spin systems.

As expected, the $^1J_{Rh,P}$ couplings (P is part of the P^S(O)$_x$ ligands) were in a similar range as those of the analogous neutral complexes **6**–**11**. Only in complexes **13a** and **14a** the formation of a four-membered RhPCS cycle led to a decrease of the $^1J_{Rh,P}$ coupling constants by 30.6 Hz (**13a**) and 21.1 Hz (**14a**), respectively. Moreover, in complexes **13a** and **14a** the ^{31}P resonances of the Ph_2PCH_2SPh ligand exhibited a marked highfield shift by 59.2 ppm (**13a**) and 47.2 ppm (**15a**) compared to the respective neutral complexes **6a** and **7a** (Table 1). These pronounced highfield shifts are also found in structurally similar rhodium complexes having bound a dppm-κ^2*P*,*P*′ ligand (four-membered RhP_2C ring) [29,36,37]. Furthermore, the formation of the four-membered rhodacycles led to a, respectively, strong ($\Delta\delta_C$ 76.3 ppm, **13a**) and a reasonable ($\Delta\delta_C$ 28.3 ppm, **14a**) lowfield shift of the α-C resonances whereas the κ*P*,κ*O* and κ*P*,κ*S* coordination of the P^S(O)$_x$ ligands in all other complexes had only little effect on the ^{13}C NMR shifts of the α-carbon atoms ($\Delta\delta \leq 7$ ppm) compared to the neutral rhodium complexes **6**–**11**.

Table 2
Selected NMR spectroscopic data (δ in ppm, J in Hz) for complexes [Rh{$Ph_2P(CH_2)_{n-1}C_\alpha H_2S(O)_xPh$-κ*P*,κ*S*/*O*}$L_2$][$BF_4$] (**13**–**18**).

	L_2 = cod					L_2 = dppe			
	n/x	$\delta_{\alpha\text{-C}}$ ($^mJ_{P,C}$)	δ_P ($^1J_{Rh,P}$)	$\delta_{C=C}$[a] ($^1J_{Rh,C}$)		n/x	$\delta_{\alpha\text{-C}}$ ($^mJ_{P,C}$)	δ_P ($^1J_{Rh,P}$)	$\delta_{P'}$[b] ($^1J_{Rh,P'}$)
13a	1/0	107.7 (7.3)[c]	−31.1 (119.5)	86.5 (9.3)	**14a**	1/0	60.3 (19.3)[c]	−22.8 (111.1)	69.1 (166.6)
13b	1/1	57.4 (10.2)[c]	53.6 (162.7)	69.4/74.1 (13.9/14.5)	**14b**	1/1	56.6 (s)	55.5 (146.3)	74.0 (182.4)
13c	1/2	57.2 (10.0)[c]	25.3 (149.0)	72.4 (14.3)	**14c**	1/2	56.4 (s)	27.1 (129.7)	76.2 (184.7)
15a	2/0	37.5 (7.2)[d]	59.0 (147.2)	87.7 (10.8)	**16a**	2/0	39.2 (10.9)[d]	59.4 (135.3)	65.5 (151.2)
15b	2/1	52.9 (s)	52.7 (135.8)	78.0/78.3 (8.1/11.3)	**16b**	2/1	60.3 (9.5)[d]	57.8 (136.4)	60.1 (145.1)
15c	2/2	51.9 (s)	18.9 (149.5)	71.1 (15.6)	**16c**	2/2	52.4 (6.4)[d]	16.5 (136.6)	77.4 (204.5)
17a	3/0	39.3 (3.6)[e]	12.4 (140.0)	86.0 (11.2)	**18a**	3/0	35.9 (8.8)[e]	7.1 (131.1)	66.4 (160.0)
17b	3/1	57.7 (4.8)[e]	11.0 (140.0)	94.5/99.0 (10.0/8.4)	**18b**	3/1	58.7 (7.6)[e]	7.7 (132.2)	60.0 (148.2)
17c	3/2	57.0 (3.8)[e]	24.2 (147.8)	71.6 (15.3)	**18c**	3/2	–	21.2 (127.0)	70.5 (182.5)

[a] C=C is part of the cod ligand and *trans* to S and O, respectively.
[b] P′ is part of the dppe ligand and *trans* to S and O, respectively.
[c] $m = 1$.
[d] $m = 2$.
[e] $m = 3$.

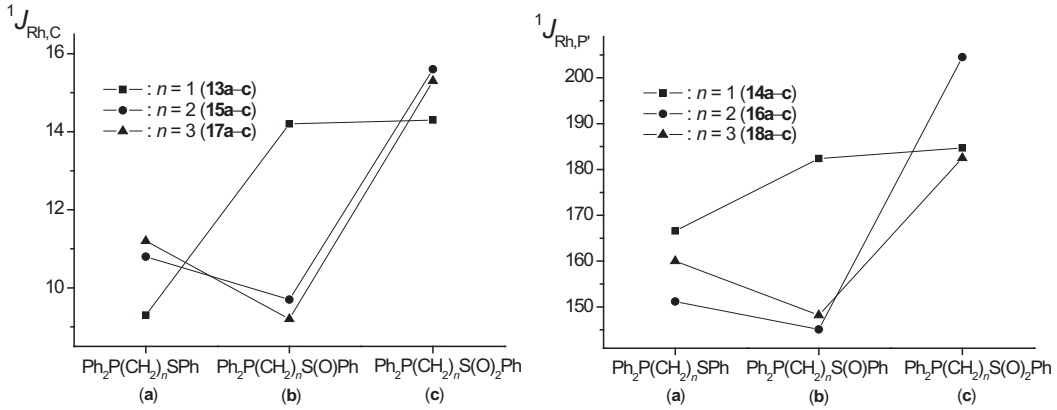


Fig. 1. Graphical representation of $^1J_{Rh,C}$ couplings in complexes **13**, **15**, **17** (left) and $^1J_{Rh,P'}$ couplings in complexes **14**, **16**, **18** (right). In complexes **13b**, **15b** and **17b** the mean value of the two $^1J_{Rh,C}$ couplings are given.

The different trans influences of the R_2S group (*S* donor) and the R_2SO_2 group (*O* donor) allowed an assignment of the coordination mode (κ*P*,κ*S* versus κ*P*,κ*O*) of the ω-phosphinofunctionalized alkyl phenyl sulfoxide ligands in complexes **13b**–**18b**. In Fig. 1, the magnitudes of the $^1J_{Rh,C}$ (C is *trans* to S/O) and $^1J_{Rh,P'}$ (P′ is *trans* to S/O) couplings of the complexes bearing sulfinylfunctionalized ligands ($x = 1$) are compared to those of the analogous complexes having bound functionalized sulfide ($x = 0$) and sulfone ($x = 2$) ligands where the κ*P*,κ*S* and κ*P*,κ*O* coordination, respectively, is obvious (Fig. 1).

As it can be seen, the two rhodium complexes having bound the $Ph_2PCH_2S(O)Ph$ ligand (**13b**, **14b**) most likely adopt a κ*P*,κ*O* coordination thus avoiding a strained four-membered ring whereas the other sulfoxide ligands in complexes **15b**, **16b**, **17b** and **18b** most probably exhibit a κ*P*,κ*S* coordination mode. For **15b** this is in full accordance with the result of the single-crystal X-ray diffraction analysis (vide infra, Fig. 2).

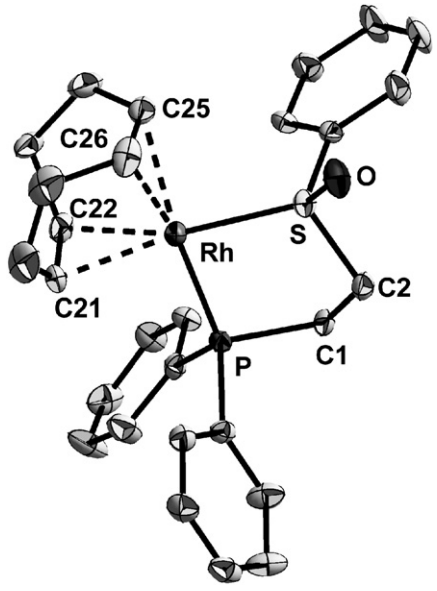


Fig. 2. Molecular structure of the cation in crystals of [Rh{$Ph_2PCH_2CH_2S(O)Ph$-κ*P*,κ*S*}(cod)][BF_4] (**15b**). The ellipsoids are shown with a probability of 30%. H atoms have been omitted for clarity. Selected structural parameters (distances in Å, angles in °): Rh–P 2.269(2), Rh–C21/22_{cg} (cg = center of gravity) 2.0868(5), Rh–C25/26_{cg} 2.1425(5), Rh–S 2.270(2), C21–C22 1.361(9), C25–C26 1.346(1), S–O 1.462(5), P–Rh–S 85.8(5), P–Rh–C21/22_{cg} 94.6(1), C21/22_{cg}–Rh–C25/26_{cg} 85.7(1), C25/26_{cg}–Rh–S 94.1(1), C25/26_{cg}–Rh–P 179.1(1), C21/22_{cg}–Rh–S 173.0(1).

In the ^{31}P NMR spectrum of the trinuclear complex **12**·4THF the resonances of two magnetically inequivalent phosphorus atoms appeared as ddd patterns from which the $^1J_{Rh,P}$ (140.7/180.3 Hz), $^2J_{P,P}$ (35.3/35.3 Hz) and $^2J_{Rh,P}$ (2.5/3.5 Hz) couplings could be obtained. Apart from the THF signals and the resonances in the aromatic region the ^1H NMR spectrum showed one broad singlet at 2.78 ppm whereas in the ^{13}C NMR spectrum two doublet patterns (δ_C 31.6/42.5 ppm) appeared showing $^1J_{P,C}$ couplings (27.8/26.7 Hz). The solid-state structure of this complex (vide infra, Fig. 4) let expect the AA′EE′ part of an AA′EE′MM′X spin system (A, E = ^{31}P; M, X = ^{103}Rh) in the ^{31}P NMR spectrum. An analysis with the PERCH software revealed that due to small $^3J_{Rh,P}$ and $^4J_{P,P}$ long-range couplings (<2 Hz) the NMR spectrum is simplified, hence two ddd patterns are found only, which is in full accord with the experimental findings.

2.2.3. Organorhodium intramolecular coordination and zwitterionic complexes, [{Rh{μ-CH(SPh)PPh_2-κ*C*:κ*P*}(cod)}$_2$]

While the ^{31}P NMR spectra of the intramolecular coordination compounds bearing a dppe ligand **23** (Table 3) appeared as higher order ABCX spin systems, those of the zwitterionic rhodium complexes [Rh{$Ph_2PCHS(O)_xPh$-κ*P*,κ*S*/*O*}(dppe)] (**21**) were found to be first order AEMX spin systems (A, B, C, E, M = ^{31}P; X = ^{103}Rh). However, all cod complexes (**20**, **22**) proved to be of first order with an AX spin system.

As revealed NMR spectroscopically, the reaction of **10b** and **11b** with $NaN(SiMe_3)_2$ to form the organometallic complexes [Rh{CH{S(O)Ph}$CH_2CH_2PPh_2$-κ*C*,κ*P*}L_2] (L_2 = cod, **22b**; dppe, **23b**) with a deprotonated sulfinyl ligand and thereby having two centers of chirality (sulfur and α-C atom) proceeded diastereoselectively. This was confirmed by the presence of only one set of signals in the NMR spectra (^1H, ^{13}C, ^{31}P). Noteworthy, in the case of **22b** initially two diastereomers in an intensity ratio of about 1:1 were observed in the ^{31}P NMR spectrum of the reaction solution (δ_P 51.6/52.1 ppm; $^1J_{Rh,P}$ = 174.6/176.4 Hz). At room temperature within 2 h an isomerization took place yielding selectively only one diastereomer (δ_P 51.6 ppm). The α-carbon atoms in the cod complex **22b** appeared as dd pattern showing $^1J_{Rh,C}$ and $^2J_{P,C}$ couplings. In contrast, the signal of the C_α atom in the dppe complex (**23b**) proved to be of too high multiplicity to be resolved.

In the zwitterionic complexes **20** and **21** the signals of the α-carbon nuclei appeared as doublet ($^1J_{P,C}$) and broad singlet patterns, respectively, which excluded a coordination of the C_α atom to the rhodium atom due to the missing $^1J_{Rh,C}$ couplings. Furthermore, from the signal pattern in the ^{31}P NMR spectra (d, **20**; 3 × ddd, **21**) it could be seen that the complexes were mononuclear. On the basis

Table 3
Selected NMR spectroscopic data (δ in ppm, J in Hz) for complexes [Rh{$Ph_2PCHS(O)_xPh$-κ*P*,κ*S*/*O*}L_2] (**20**, **21**) and [Rh{$CH\{S(O)_xPh\}CH_2CH_2PPh_2$-κ*C*,κ*P*}$L_2$] (**22**, **23**).

		$Ph_2PC_\alpha HS(O)_xPh$						$Ph_2PC_\gamma H_2CH_2C_\alpha HS(O)_xPh$			
	L	*x*	$\delta_{\alpha\text{-}C}$ ($^1J_{P,C}$)	$\delta_{C=C}$[a] ($^1J_{Rh,C}$)	$\delta_{P'}$[a] ($^1J_{Rh,P'}$)		L	*x*	$\delta_{\alpha\text{-}C}$ ($^2J_{P,C}$)	$\delta_{\gamma\text{-}C}$ ($^1J_{P,C}$)	δ_P ($^1J_{Rh,P}$)
						22a[b]	cod	0	35.5 (4.5)	31.9 (22.4)	58.6 (168.3)
20b	cod	1	70.1 (14.3)	87.0/87.3 (10.1/9.7)	–	**22b**	cod	1	63.0 (4.9)	34.0 (26.9)	51.6 (174.6)
20c	cod	2	69.0 (14.7)	85.5/87.9 (9.9/9.8)	–	**22c**[c]	cod	2	63.0 (4.6)	33.0 (26.9)	52.0 (172.0)
21a[d]	dppe	0	–	–	69.4 (159.1)	**23a**[b]	dppe	0	41.9–42.8 (m)	33.6 (17.1)	58.6 (162.3)
21b	dppe	1	66.6 (s)	–	67.1 (157.3)	**23b**	dppe	1	57.9–59.8 (m)	29.3 (15.9)	58.0 (156.1)
21c	dppe	2	37.4 (s)	–	74.1 (189.0)	**23c**[c]	dppe	2	61.1–63.0 (m)	35.0 (22.2)	55.5 (153.1)

[a] *trans* to S or O, respectively.
[b] Values taken from Ref. [24].
[c] Values taken from Ref. [29].
[d] Not isolated in substance; only characterized ^{31}P NMR spectroscopically.

of these facts it was concluded that complexes **20** and **21** have the anionic [$Ph_2PCHS(O)Ph$] ligand κ*P*,κ*S* (**21a**/**b**) and κ*P*,κ*O* (**20b**/**c**, **21c**) coordinated. Since the central methine carbon atom is not coordinated to Rh, these are zwitterionic complexes as it is found in numerous structurally similar dppm$_{-H}$-κ^2*P*,*P*′ complexes [36,38,39]. Till now, in literature zwitterionic complexes with P^S ligands are described only in which the anionic carbon atom is part of a carboborane [40] or of a ring system [41]. The assignment of the coordination mode of the flexidentate anionic [$Ph_2PCHS(O)Ph$] ligand in **20b** (κ*P*,κ*O*) and **21b** (κ*P*,κ*S*) was performed on the same basis as it was done for the appropriate cationic rhodium complexes **13b** and **14b** (see Section 2.2.2.).

The ^{31}P NMR spectrum of the dinuclear complex **19** which was obtained directly from the reaction solution exhibited a higher order spectrum showing 6 lines. Considering the solid-state structure of [{Rh(μ-$Ph_2PCH(SPh)$-κ*C*:κ*P*)(cod)}$_2$]·THF (**19**·THF) (vide infra, Fig. 5) the pattern can be interpreted as an AA′XX′ spin system (A = ^{31}P, X = ^{103}Rh) showing only 6 instead of the expected 10 lines caused by a too small (<1 Hz) $^3J_{Rh,Rh}$ coupling constant. Using the PERCH software $^1J_{Rh,P}$ (169.6/167.3 Hz), $^2J_{Rh,P}$ (4.0/1.0 Hz) and $^3J_{P,P}$ (147.4 Hz) coupling constants could be identified. Complex **19**·THF, which crystallized from the reaction mixture within 24 h, could not be re-dissolved in any common solvent which prevented further NMR spectroscopic investigations.

2.3. Structures

2.3.1. Structures of [Rh{$Ph_2PCH_2CH_2S(O)_xPh$}(cod)][BF_4] (*x* = 1, ***15b***; *x* = 2, ***15c***)

Crystals of **15b** and **15c** suitable for X-ray diffraction analyses were obtained from THF solutions at room temperature. The two complexes crystallized as discrete cations and anions without unusual intermolecular interactions (shortest distance between non-hydrogen atoms: 3.323(8) Å, C2···F3′, **15b**; 3.054(5) Å, C2···F3′, **15c**). The structures of the cations are shown in Figs. 2 and 3. Selected structural parameters are given in the figure captions.

In the two complexes the rhodium atoms exhibit a slightly distorted square-planar configuration where the primary donor sets are built up by the bidentately bound cycloocta-1,5-diene ligand and, respectively, a chelating κ*P*,κ*S* coordinated β-phosphino-functionalized ethyl phenyl sulfoxide ligand (**15b**) and a chelating κ*P*,κ*O* coordinated β-phosphinofunctionalized ethyl phenyl sulfone ligand (**15c**). In the two complexes all angles between neighbored ligands are close to 90° (85.7(1)–94.6(1)°, **15b**; 87.0(1)–93.1(1)°, **15c**) and those between *trans* standing ligands are close to 180° (179.1(1)/173.0(1)°, **15b**; 178.0(1)/172.9(1)°, **15c**). The trans influence order $PR_3 > R_2SO$-κ*S* > R_2SO_2-κ*O* is clearly reflected in different Rh–C_{olefin} bond lengths. As expected, the Rh–C25/26$_{cg}$ (C25/26$_{cg}$ is *trans* to P; cg = center of gravity) bonds are of the same length (2.1433(3) Å, **15b**; 2.1425(5) Å, **15c**). However, the Rh–C21/22$_{cg}$ bond in **15b** (2.0868(5) Å, *trans* to S) is markedly longer than the analogous bond in **15c** (1.9877(3) Å, *trans* to O). Furthermore, the olefinic C–C bond *trans* to O in **15c** is considerably longer than the other three C–C double bonds *trans* to P and S in **15b**/**c** (1.413(6) Å versus 1.346 (1)–1.361(9) Å), respectively. This might be traced back to the weak trans influence of the R_2SO_2-κ*O* donor which goes along with the above mentioned short Rh–C bond; similar observations were made in other cod rhodium complexes [42–44].

2.3.2. Structure of [Rh_3(μ-Cl)(μ-Ph_2PCH_2SPh-κ*P*:κ*S*)$_4$][BF_4]$_2$·4THF (***12***·4THF)

Crystals of **12**·4THF suitable for an X-ray diffraction analysis were obtained from CH_2Cl_2 solution with a layer of *n*-pentane at room temperature. The complex crystallized as discrete [Rh_3(μ-Cl)(μ-Ph_2PCH_2SPh-κ*P*:κ*S*)$_4$]$^{2+}$ cations and [BF_4]$^-$ anions without unusual intermolecular interactions (shortest distance between non-hydrogen atoms: 3.486(9) Å, C20···O1′). The structure of the cation is

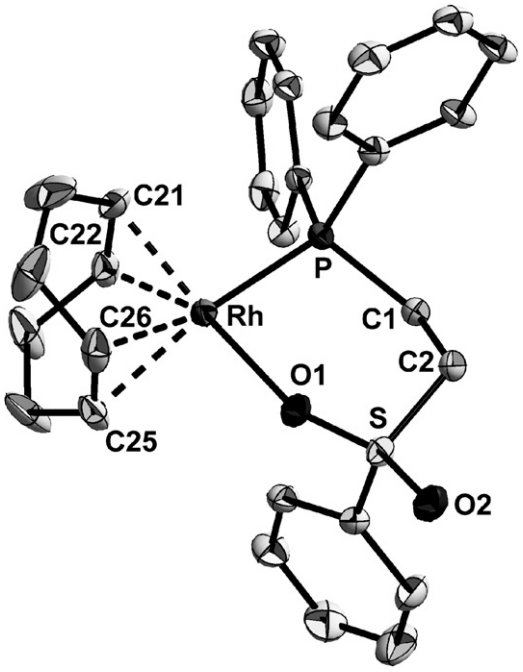


Fig. 3. Molecular structure of the cation in crystals of [Rh{$Ph_2PCH_2CH_2S(O)_2Ph$-κ*P*,κ*O*}(cod)][BF_4] (**15c**). The ellipsoides are shown with a probability of 30%. H atoms have been omitted for clarity. Selected structural parameters (distances in Å, angles in °): Rh–P 2.2859(8), Rh–C21/22$_{cg}$ 1.9877(3), Rh–C25/26$_{cg}$ 2.1433(3), Rh–O1 2.166(2), C21–C22 1.413(6), C25–C26 1.358(6), P–Rh–O1 92.2(1), P–Rh–C21/22$_{cg}$ 93.1(1), C22/23$_{cg}$–Rh–C25/26$_{cg}$ 87.0(1), C25/26$_{cg}$–Rh–O1 87.9(1), C25/26$_{cg}$–Rh–P 178.0(1), C21/22$_{cg}$–Rh–O1 172.9(1).

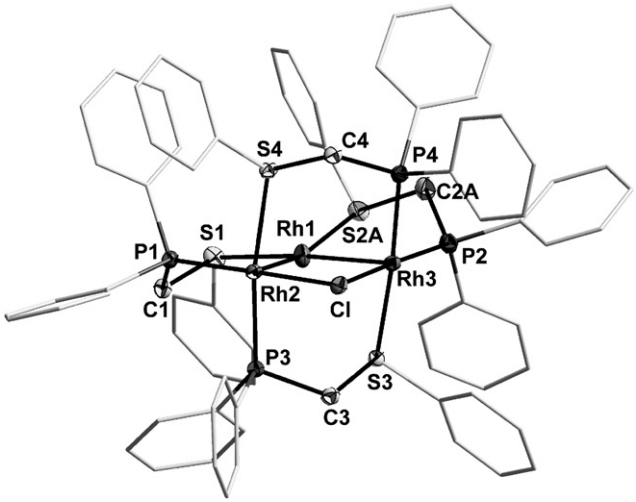


Fig. 4. Molecular structure of the cation in crystals of $[Rh_3(\mu\text{-}Cl)(\mu\text{-}Ph_2PCH_2SPh\text{-}\kappa P{:}\kappa S)_4][BF_4]_2\cdot 4THF$ (**12**·4THF). The ellipsoides are shown with a probability of 30%. For clarity, H atoms have been omitted and phenyl rings are displayed as wire model. One CH_2SPh group (C2A/S2A and C2B/S2B) was found to be disordered over two positions with an occupancy of 58.8(4) and 41.2(4)%; only the major occupied position is shown. Selected structural parameters (distances in Å, angles in °): Rh1–Rh2 2.7357 (5), Rh1–Rh3 2.7606(5), Rh2–Cl 2.406(1), Rh3–Cl 2.415(1), Rh1–S2A 2.637(2), Rh1–S2B 2.458(3), Rh1–S1 2.553(1), Rh2–P1 2.266(1), Rh2–P3 2.276(1), Rh2–S4 2.401(1), Rh3–P2 2.249(1), Rh3–P4 2.288(1), Rh3–S3 2.371(1), Rh2–Rh1–Rh3 74.06 (1), Rh1–Rh2–Cl 99.85(3), Rh1–Rh3–Cl 98.92(3), Rh2–Cl–Rh3 86.72(3), Rh1–Rh2–S1 101.63(3), Rh1–Rh2–P1 84.02(3), P1–Rh2–Cl 176.13(4), S4–Rh2–P3 170.65(5), P2–Rh3–Cl 175.62(4), P4–Rh3–S3 172.85(4), Rh1–Rh2···Rh3–Cl 173.38 (4).

shown in Fig. 4. Selected structural parameters are given in the figure caption.

The cation is built up by a four-membered Rh_3Cl cycle and four μ-Ph_2PCH_2SPh-$\kappa P{:}\kappa S$ ligands. The overall disposition of the ligands is consistent with a C_2 symmetry (axis through Rh1 and Cl) in rough approximation. The central rhodium atom (Rh1) adopts a distorted square-planar configuration where the primary donor set is built up by two *cis* standing sulfur atoms of two μ-Ph_2PCH_2SPh ligands and by the other two rhodium atoms Rh2 and Rh3. In contrast, these two rhodium atoms exhibit a square-pyramidal configuration having Rh1 in the apical position each. The equatorial positions are occupied by the μ-Cl ligand as well as by two *cis* standing phosphorus atoms and one sulfur atom. The torsion angle Rh1–Rh2···Rh3–Cl is 173.38(4)°, thus the four-membered ring is almost planar. Regarding the Rh_3Cl cycle, the Cl–Rh2–Rh1 (99.85(3)°) and the Cl–Rh3–Rh1 (98.92(3)°) angles are of a similar size whereas the Rh2–Rh1–Rh3 (74.06(1)°) and the Rh2–Cl–Rh3 (86.72(3)°) angles are considerably smaller. The two five-membered rhodacycles Rh1–S1–C1–P1–Rh2 and Rh1–S2A–C2A–P2–Rh3/Rh1–S2B–C2B–P2–Rh3 adopt a half-chair conformation twisted on P1 and C1 as well as on P2 and C2A/C2B, respectively. Even though the Rh1–Rh2 bond (2.7357(5) Å) is shorter than the Rh1–Rh3 bond (2.7606(5) Å), both are in the expected range for Rh–Rh bonds (median: 2.760 Å, lower/higher quartile: 2.682/2.822 Å, $n = 4446$; n = number of observations) [45]. The distances between Rh2 and Rh3 (3.3100(5) Å) as well as between Rh1 and Cl (3.940(1) Å) exclude any interactions between these atoms.

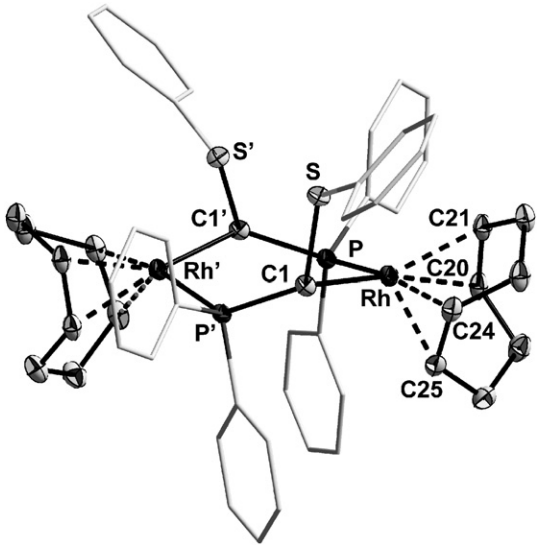


Fig. 5. Molecular structure of $[\{Rh\{\mu\text{-}CH(SPh)PPh_2\text{-}\kappa C{:}\kappa P\}(cod)\}_2]$ (**19**) in crystals of **19**·THF. The ellipsoides are shown with a probability of 30%. For clarity, H atoms have been omitted and phenyl rings are displayed as wire model. Selected structural parameters (distances in Å, angles in °): Rh–P 2.3429(8), Rh–C1 2.077(2), Rh–C20/21_{cg} 2.0979(3), Rh–C24/25_{cg} 2.0625(3), C1–Rh–P 95.42(7), P–Rh–C20/21_{cg} 93.24(2), C20/21_{cg}–Rh–C24/25_{cg} 85.23(1), C24/25_{cg}–Rh–C1 90.42(1), S–C1–Rh 81.5(1), C20/21_{cg}–Rh–C1, 169.05(6); C24/25_{cg}–Rh–P, 150.93(2).

2.3.3. Structure of $[\{Rh\{\mu\text{-}CH(SPh)PPh_2\text{-}\kappa C{:}\kappa P\}(cod)\}_2]\cdot THF$ (**19**·THF)

Crystals of **19**·THF suitable for an X-ray diffraction analysis were obtained from THF solution at room temperature. The complex crystallized as discrete dinuclear entities and between them no unusual intermolecular contacts were found (shortest intermolecular distance between non-hydrogen atoms is 4.09(2) Å, C25···C12″). The dinuclear complex exhibits crystallographically imposed C_2 symmetry. The structure is shown in Fig. 5, selected structural parameters are given in the figure caption. The rhodium atoms are in a distorted square-planar geometry and surrounded by a bidentately bound cycloocta-1,5-diene ligand as well as by a sulfur and a carbon atom of the μ-CH(SPh)PPh_2-$\kappa C{:}\kappa P$ ligand. Due to the higher trans influence of the anionic C ligand compared to the neutral P ligand the Rh–C20/21_{cg} bond (2.0979(3) Å, *trans* to C) is markedly longer than the Rh–C24/25_{cg} bond (2.0625(3) Å, *trans* to P). The six-membered $Rh_2C_2P_2$ ring adopts a twist-boat conformation having the SPh groups almost perpendicular to it. Notably, there is a weak interaction between the rhodium and the sulfur atom (Rh···S = 2.5449(8) Å) giving rise to a pseudo-five-coordination [46] which results in a severe distortion from the ideal square-planar geometry (C20/21_{cg}–Rh–C1, 169.05(6)°; C24/25_{cg}–Rh–P, 150.93(2)°).

2.3.4. Structures of calculated zwitterionic complexes

To get insight into the coordination mode of the flexidentate $[Ph_2PCHS(O)Ph]$ ligand ($\kappa P,\kappa S$ versus $\kappa P,\kappa O$), quantum chemical calculations on the DFT level of theory were performed. The calculated structures of the two isomeric zwitterionic complexes with a cod coligand $[Rh\{Ph_2PCHS(O)Ph\text{-}\kappa P,\kappa S/O\}(cod)]$ (**20b**$_{calc}$, **20b**′$_{calc}$) are shown in Fig. 6. The complex with the $\kappa P,\kappa O$ coordination (**20b**$_{calc}$) possessing a five-membered RhPCSO cycle was found to be energetically more stable by 4.4 kcal/mol (Gibbs free energy at 298 K) than the constitutional isomer $[Rh\{Ph_2PCHS(O)Ph\text{-}\kappa P,\kappa S\}(cod)]$ (**20b**′$_{calc}$). This is in full accordance with the experimental findings.

In addition, for structural comparison, the protonated congeners $[Rh\{Ph_2PCH_2S(O)Ph\text{-}\kappa P,\kappa O\}(cod)]^+$ (**13b**$_{calc}$) and $[Rh\{Ph_2PCH_2S(O)Ph\text{-}\kappa P,\kappa S\}(cod)]^+$ (**13b**′$_{calc}$) have been calculated. Thus, complex **13b**$_{calc}$ represents the calculated cation of the isolated complex $[Rh\{Ph_2CH_2S(O)Ph\text{-}\kappa P,\kappa O\}(cod)][BF_4]$ (**13b**). In both complexes the deprotonation of the CH_2 group goes along with a considerable shortening of the P–C bonds (1.758/1.741 Å, **20b**$_{calc}$/**20b**′$_{calc}$) and the S–C bonds (1.674/1.687 Å, **20b**$_{calc}$/**20b**′$_{calc}$) compared to their

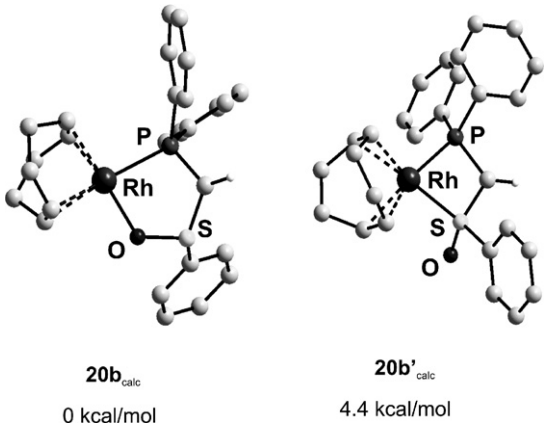


Fig. 6. Calculated structures of [Rh{$Ph_2PCHS(O)Ph$-κ*P*,κ*O*}(cod)] (**20b**$_{calc}$) and [Rh{$Ph_2PCHS(O)Ph$-κ*P*,κ*S*}(cod)] (**20b**′$_{calc}$). For clarity, only the H atoms of the methine carbon atoms are displayed. Gibbs free energy of **20b**′$_{calc}$ is relative to that of **20b**$_{calc}$.

protonated congeners (P–C: 1.880/1.867 Å; S–C: 1.827/1.839 Å; **13b**$_{calc}$/**13b**′$_{calc}$). Such a shortening of the P–C bonds is also found in complexes bearing an anionic dppm$_{-H}$-κ^2*P*,*P*′ ligand which is explained in terms of an ylidic bonding model with some charge delocalization within the PCP moiety [47]. Moreover, the fact that the calculated complex with the κ*P*,κ*O* coordinated ligand (**13b**$_{calc}$) is the thermodynamically favored isomer ($\Delta\Delta G^{\ominus}$ = 10.7 kcal/mol; see Supplemental Material, Figure S 3) is in full accordance with the assignment of the coordination mode of the $Ph_2CH_2S(O)Ph$ ligand in complex [Rh{$Ph_2CH_2S(O)Ph$-κ*P*,κ*O*}(cod)][BF_4] (**13b**) which was done on the basis of the magnitudes of the $^1J_{Rh,C}$ coupling constants (see Section 2.2.2).

For the dppe complex **21b** the two calculated constitutional isomers [Rh{$Ph_2PCHS(O)Ph$-κ*P*,κ*O*}(dppe)] (**21b**$_{calc}$) and [Rh{$Ph_2PCHS(O)Ph$-κ*P*,κ*S*}(dppe)] (**21b**′$_{calc}$; see Supplemental Material, Figure S 1) were found to be of the same energy within the margin of error ($\Delta\Delta G^{\ominus}$ = 0.1 kcal/mol), thus the proposed coordination mode based on NMR spectroscopic investigations (κ*P*,κ*S*) could be neither validated nor invalidated. Additionally, the analogous dmpe complexes ([Rh{$Ph_2PCHS(O)Ph$-κ*P*,κ*O*}(dmpe)], **24**$_{calc}$; [Rh{$Ph_2PCHS(O)Ph$-κ*P*,κ*S*}(dmpe)], **24**′$_{calc}$) were calculated and found to be of the same energy, too ($\Delta\Delta G^{\ominus}$ = 0.2 kcal/mol; see Supplemental Material, Figure S 2).

2.4. Conclusions

From the experimental investigations and quantum chemical calculations performed in this work the following conclusions on the coordination behavior of ω-diphenylphosphinofunctionalized sulfide (x = 0), sulfoxide (x = 1) and sulfone (x = 2) ligands (type **I**, Chart 2) and their deprotonated congeners (type **II**) can be drawn:

1. Reactions of [$(RhL_2)_2(\mu\text{-}Cl)_2$] with type **I** sulfoxide ligands (x = 1) followed by the addition of Ag[BF_4] give rise to the formation of cationic complexes of the type [Rh{$Ph_2P(CH_2)_n$S(O)Ph-κ*P*,κ*S*/*O*}L_2][BF_4] (**13**–**18**). While the ligands with the dimethylene (n = 2) and the trimethylene (n = 3) spacer exhibit a κ*P*,κ*S* coordination, those with the methylene spacer (n = 1) afford a κ*P*,κ*O* coordination. In all cases thermodynamically favored five- and six-membered rhodacycles are formed. Thus, phosphinofunctionalized sulfoxides are flexidentate ligands (κ*P*,κ*S* versus κ*P*,κ*O*). Here the coordination mode is dependent on the ring size and not on the Lewis basicity of the coligand (cod, dppe), as it is described for non-functionalized sulfoxides [20] as well as for *N*-phosphino sulfinamide ligands (PNSO-type ligands) [48].
2. In contrast, type **I** sulfide (x = 0) and sulfone ligands (x = 2) are not flexidentate. Thus, in the respective complexes [Rh{$Ph_2P(CH_2)_n$SPh-κ*P*,κ*S*}L_2][BF_4] (**13a**–**18a**) and [Rh{$Ph_2P(CH_2)_nS(O)_2Ph$-κ*P*,κ*O*}L_2][BF_4] (**13c**–**18c**) also four- (n = 1, **13a**/**14a**) and seven-membered (n = 3, **17c**/**18c**) rhodacycles are yielded. The *O* coordination of the sulfonyl group was unambiguously proved by the solid-state structure in case of **15c**, being one of the few structurally characterized complexes bearing sulfone ligands which is attributed to their low donor capability [49].
3. The weaker coordination capability of the cod ligand compared to the dppe ligand is evident in the reaction of the rhodium complex bearing a κ*P* coordinated type **I** ligand (x = 0, n = 1, **6a**) with Ag[BF_4] leading, with cleavage of the cod ligand, to the formation of the trinuclear Rh(I) complex [$Rh_3(\mu\text{-}Cl)(\mu\text{-}Ph_2PCH_2SPh$-κ*P*:κ*S*)$_4$][$BF_4$]$_2$·4THF (**12**·4THF). Noteworthy, **12**·4THF contains the structural motif of an A-frame complex (P1–Rh2–μ-Cl–Rh–P2) which is well known from complexes with dppm ligands [50,51]. The formal addition of Rh1 to that structural unit results in two five-coordinated Rh centers (Rh2, Rh3). The four-membered Rh_3Cl cycle as structural unit in complex **12**·4THF is only found in one further complex, namely in an osmium–rhodium carbonyl cluster [52].
4. Type **II** ligands with a C_3 spacer (n = 3) are found to form organorhodium intramolecular coordination compounds (**22**, **23**) irrespective of the nature of the sulfur functionalization (x = 0–2) [24,29]. In the case of the sulfinylfunctionalized ligands (x = 1) the deprotonation of the prochiral CH_2 group creates a second chiral center; noteworthy, the formation of the respective organorhodium complexes (**22b**, **23b**) proved to be diastereoselective. The diastereoselective synthesis of metallacycles [53–55] and their use as catalysts [56,57] have been described in literature previously.
5. In contrast, the anionic type **II** ligands with a C_1 spacer (n = 1) are found to form zwitterionic complexes containing both four- and five-membered rhodacycles. Interestingly, the coordination of the flexidentate sulfinyl group was found to be dependent on the coligand: With the more strongly electron donating dppe coligand a κ*P*,κ*S* coordination of the [$Ph_2PCHS(O)Ph$] ligand was found, whereas the cod coligand causes a κ*P*,κ*O* coordination. Such a coligand-dependency on the coordination mode of sulfoxide ligands has been discussed on the basis of the HSAB theory [58]. A marked influence of the coligand was also found in the complexes bearing the anionic [$Ph_2PCHSPh$] ligand: With dppe a zwitterionic complex (**21a**) was formed as described above, whereas with cod a dinuclear complex (**19**·THF) was yielded having coordinated μ-$Ph_2PCHSPh$-κ*C*:κ*P* ligands. Yet the only structurally similar dinuclear rhodium complex described in literature is the Rh(III) complex [{Rh(Cp^*)Me(μ-PMe_2CH_2-κ*C*:κ*P*)}$_2$] [59].

These investigations show the versatile coordination behavior of bidentate neutral P^S(O)$_x$ ligands of type **I** (Chart 2) and their deprotonated congeners (type **II**) which can be understood in terms of the type of the sulfur functionality (sulfanyl versus sulfinyl versus sulfonyl) and the length of the spacer between the two coordination centers (κ*P*,κ*S*; κ*P*,κ*O*; κ*C*,κ*P*). Thus, these ligands offer an easy access to formation of novel cationic rhodium complexes,

$Ph_2P-(CH_2)_n-S(O)_xPh$ (**I**) $\qquad$ $Ph_2P-(CH_2)_{n-1}-\overset{\ominus}{C}H-S(O)_xPh$ (**II**)

Chart 2. ω-Diphenylphosphinofunctionalized sulfides (x = 0), sulfoxides (x = 1) and sulfones (x = 2) **I** (n = 1–3) and their deprotonated congeners **II** being used as ligands in Rh(I) complexes.

organorhodium intramolecular coordination compounds as well as zwitterionic rhodium complexes.

3. Experimental part

3.1. General comments

All reactions and manipulations were carried out under argon using standard Schlenk techniques. Diethyl ether, toluene, *n*-pentane, THF were dried over Na/benzophenone, CH_2Cl_2 over CaH_2 and freshly distilled prior to use. NMR spectra (^1H, ^{13}C, ^{31}P) were recorded at 27 °C on Varian Gemini 200, VXR 400, and Unity 500 spectrometers. Chemical shifts are relative to solvent signals ($CDCl_3$, δ_H 7.24, δ_C 77.0; CD_2Cl_2, δ_H 5.32, δ_C 53.8; C_6D_6, δ_H 7.15, δ_C 128.0; THF-d_8, δ_H 1.73/3.58, δ_C 25.4/67.6) as internal references; δ (^{31}P) is relative to external H_3PO_4 (85%). Multiplets in NMR spectra of higher order resulting in pseudo doublets and triplets are denoted by 'd' and 't', respectively; the distance between the outer lines is given as *N*. Coupling constants $J_{P,P}$ and $J_{P,Rh}$ from higher order multiplets were obtained by using the PERCH NMR software package. For couplings in ring systems only the shortest coupling path is given. Microanalyses were performed in the Microanalytical Laboratory of the University of Halle using a CHNS-932 (LECO) elemental analyzer. The high-resolution ESI mass spectra were obtained from a Bruker Apex III Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer (Bruker Daltonics) equipped with an Infinity cell, a 7.0 T superconducting magnet (Bruker), a rf-only hexapole ion guide, and an external APOLLO electrospray ion source (Agilent, off-axis spray). The sample solutions were introduced continuously via a syringe pump with a flow rate of 120 μL h^{-1}. Details of the preparation of starting compounds and a complete set of their NMR spectroscopic data are given in the Supplemental Material. [{Rh(cod)}$_2$(μ-Cl)$_2$] (**4**), [{Rh(dppe)}$_2$(μ-Cl)$_2$] (**5**), $Ph_2PCH_2CH_2CH_2SPh$ (**3a**) and $Ph_2PCH_2CH_2CH_2S(O)_2Ph$ (**3c**) were prepared according to literature procedures [24,29,60,61].

3.2. Preparation of [RhCl{$Ph_2P(CH_2)_nS(O)_xPh$-κP}L_2] (**6**–**11**)

At −78 °C to a stirred solution of [(RhL_2)$_2$(μ-Cl)$_2$] (L_2 = cod, **4**; dppe, **5**; 0.25 mmol) in CH_2Cl_2 (5 mL) $Ph_2P(CH_2)_nS(O)_xPh$ (0.50 mmol) dissolved in CH_2Cl_2 (2 mL) was added via a syringe and the mixture was stirred for 1 h at room temperature. The solution was concentrated under reduced pressure to half of its volume before *n*-pentane (5 mL) was added. The resulted precipitate was filtered off, washed with *n*-pentane (3 × 5 mL) and dried in vacuo.

L_2 = cod, n = 1, x = 0 (**6a**). Yield: 228 mg (82%). HRMS (ESI): *m*/*z* Calcd. for $[C_{27}H_{29}PRhS]^+$: 519.0778; found for $[M-Cl]^+$: 519.0771. ^1H NMR (400 MHz, $CDCl_3$): δ 1.90–2.02/2.35 (m/s, –/br, 4H/4H, 4× CH_2, cod), 3.04/5.54 (s/s, br/br, 2H/2H, 4× C*H*, cod), 4.12 (d, $^2J(^{31}P,^1H)$ = 5.6 Hz, 2H, CH_2SPh), 7.08–7.79 (m, 15H, H_{Ph}). ^{13}C NMR (100 MHz, $CDCl_3$): δ 28.8/33.0 (s/s, br/br, 4× CH_2, cod), 31.4 (d, $^1J(^{13}C,^{31}P)$ = 17.8 Hz, CH_2SPh), 70.7/105.8 (s/s, br/br, 4× C*H*, cod), 126.2–137.1 (C_{Ph}). ^{31}P NMR (81 MHz, $CDCl_3$): δ 28.1 (d, $^1J(^{103}Rh,^{31}P)$ = 150.1 Hz, PPh_2).

L_2 = cod, n = 1, x = 1 (**6b**). Yield: 257 mg (90%). HRMS (ESI): *m*/*z* Calcd. for $[C_{27}H_{29}OPRhS]^+$: 535.0726; found for $[M-Cl]^+$: 535.0723. ^1H NMR (400 MHz, $CDCl_3$): δ 1.88–2.18/2.46 (m/s, –/br, 4H/4H, 4× CH_2, cod), 3.20/3.29/5.61/5.65 (s/s/s/s, br/br/br/br, 1H/1H/1H/1H, 4× C*H*, cod), 3.86/4.08 (dd/dd, $^2J(^{31}P,^1H)$ = 9.1/8.0 Hz, $^2J(^1H,^1H)$ = 13.5/13.5 Hz, 1H/1H, CH_2SOPh), 7.32–7.87 (m, 15H, H_{Ph}). ^{13}C NMR (100 MHz, $CDCl_3$): δ 28.9/29.2/32.8/33.4 (s/s/s/s, br/br/br/br, 4× CH_2, cod), 62.3 (d, $^1J(^{13}C,^{31}P)$ = 18.3 Hz, CH_2SOPh), 70.4/72.6/106.6/108.0 (m/m/s/s, –/–/br/br, 4× C*H*, cod), 123.9–146.7 (C_{Ph}). ^{31}P NMR (81 MHz, $CDCl_3$): δ 30.8 (d, $^1J(^{103}Rh,^{31}P)$ = 151.2 Hz, PPh_2).

L_2 = cod, n = 1, x = 2 (**6c**). Yield: 258 mg (88%). HRMS (ESI): *m*/*z* Calcd. for $[C_{27}H_{29}O_2PRhS]^+$: 551.0675; found for $[M-Cl]^+$: 551.0673. ^1H NMR (400 MHz, CD_2Cl_2): δ 1.91–1.95/2.04–2.11/2.41 (m/m/m, 2H/2H/4H, 4× CH_2, cod), 3.16/5.50 (s/s, br/br, 2H/2H, 4× C*H* (cod)), 4.60 (d, $^2J(^{31}P,^1H)$ = 7.4 Hz, CH_2SO_2Ph), 7.41–8.00 (m, 15H, H_{Ph}). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 28.9/32.9 (s/s, br/br, 4× CH_2, cod), 54.9 (d, $^1J(^{13}C,^{31}P)$ = 6.8 Hz, CH_2SO_2Ph), 71.3/105.1 (d/dd, $^1J(^{103}Rh,^{13}C)$ = 13.6/12.2 Hz, $^2J(^{31}P_{trans},^{13}C)$ = 7.4 Hz, 4× C*H*, cod), 127.7–142.1 (C_{Ph}). ^{31}P NMR (81 MHz, CD_2Cl_2): δ 24.0 (d, $^1J(^{103}Rh,^{31}P)$ = 154.1 Hz, PPh_2).

L_2 = cod, n = 2, x = 0 (**8a**). Yield: 211 mg (72%). HRMS (ESI): *m*/*z* Calcd. for $[C_{28}H_{31}PRhS]^+$: 533.4900; found for $[M-Cl]^+$: 533.4907. ^1H NMR (400 MHz, CD_2Cl_2): δ 1.61–1.82/2.35 (m, 8H, 4× CH_2, cod), 2.53 (s, br, 2H, CH_2PPh$_2$), 2.74–2.81 (m, CH_2SPh), 4.13 (s, br, 4H, 4× C*H*, cod), 7.26–7.40 (m, 15H, H_{Ph}). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 31.1 (s, 4× CH_2, cod), 31.4 (d, $^1J(^{31}P,^{13}C)$ = 15.9 Hz, CH_2PPh$_2$), 36.9 (d, $^2J(^{31}P,^{13}C)$ = 7.2 Hz, CH_2SPh), 76.6 (m, 4× C*H*, cod), 128.5–133.4 (C_{Ph}). ^{31}P NMR (202 MHz, CD_2Cl_2): δ 26.1 (d, $^1J(^{103}Rh,^{31}P)$ = 150.7 Hz, PPh_2).

L_2 = cod, n = 2, x = 1 (**8b**). Yield: 252 mg (89%). HRMS (ESI): *m*/*z* Calcd. for $[C_{28}H_{31}OPRhS]^+$: 549.4894; found for $[M-Cl]^+$: 549.4888. ^1H NMR (400 MHz, CD_2Cl_2): δ 1.60/2.34 (m/m, 4H/4H, 4× CH_2 (cod)), 2.54 (m, 2H, CH_2PPh$_2$), 2.73–2.83 (m, 2H, CH_2SOPh), 4.12 (s, br, 4H, 4× C*H* (cod)), 7.24–7.40 (m, 15H, H_{Ph}). ^{13}C NMR (125 MHz, CD_2Cl_2): δ 20.1 (d, $^1J(^{31}P,^{13}C)$ = 22.9 Hz, CH_2PPh$_2$), 31.1/31.3 (s/s, br/br, 4× CH_2, cod), 52.9 (s, br, CH_2SOPh), 71.2/106.4 (d/s, –/br, $^1J(^{103}Rh,^{13}C)$ = 14.2 Hz, 4× C*H*, cod), 106.4–140.5 (C_{Ph}). ^{31}P NMR (202 MHz, CH_2Cl_2): δ 26.8 (d, $^1J(^{103}Rh,^{31}P)$ = 151.2 Hz, PPh_2).

L_2 = cod, n = 2, x = 2 (**8c**). Yield: 252 mg (89%). HRMS (ESI): *m*/*z* Calcd. for $[C_{28}H_{31}O_2PRhS]^+$: 565.4888; found for $[M-Cl]^+$: 565.4874. ^1H NMR (400 MHz, CD_2Cl_2): δ 1.89/2.02/2.29 (m/m/m, 2H/2H/4H, 4× CH_2, cod), 2.75–2.82 (m, 2H, CH_2PPh$_2$), 3.73–3.79 (m, CH_2SO_2Ph), 2.95/5.43 (s/s, br/br, 2H/2H, 4× C*H* (cod)), 7.32–7.89 (m, 15H, H_{Ph}). ^{13}C NMR (125 MHz, CD_2Cl_2): δ 22.6 (d, $^1J(^{31}P,^{13}C)$ = 23.6 Hz, CH_2PPh$_2$), 29.5/33.7 (s/s, 4× CH_2, cod), 53.5 (d, $^2J(^{31}P,^{13}C)$ = 2.7 Hz CH_2SO_2Ph), 71.2/106.4 (d/s, –/br, $^1J(^{103}Rh,^{13}C)$ = 14.2 Hz, 4× C*H*, cod), 106.4–140.5 (C_{Ph}). ^{31}P NMR (202 MHz, THF-d_8): δ 24.7 (d, $^1J(^{103}Rh,^{31}P)$ = 153.2 Hz, PPh_2).

L_2 = cod, n = 3, x = 1 (**10b**). Yield: 270 mg (90%). HRMS (ESI): *m*/*z* Calcd. for $[C_{29}H_{33}OPRhS]^+$: 563.5160; found for $[M-Cl]^+$: 563.5169. ^1H NMR (400 MHz, CD_2Cl_2): δ 1.92–1.99/2.27–2.40 (m/m, 4H/6H, 4× CH_2 (cod), CH_2CH$_2$PPh$_2$), 2.44–2.55/2.65–2.74 (m/m, 1H/1H, CH_2PPh$_2$), 2.89–2.96/3.19–3.27 (m/m, 1H/1H, CH_2SOPh), 4.14 (m, 4H, 4× C*H*, cod), 7.34–7.71 (m, 15H, H_{Ph}). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 19.8 (d, $^2J(^{31}P,^{13}C)$ = 2.9 Hz, CH_2CH$_2$PPh$_2$), 26.9 (d, $^1J(^{31}P,^{13}C)$ = 25.3 Hz, CH_2PPh$_2$), 31.1/31.3 (s/s, 4× CH_2 (cod)), 58.0 (d, $^3J(^{13}C,^{31}P)$ = 12.1 Hz, CH_2SOPh), 87.7 (s, br, 4× C*H*, cod), 124.4–144.6 (C_{Ph}). ^{31}P NMR (81 MHz, CD_2Cl_2): δ 26.8 (d, $^1J(^{103}Rh,^{31}P)$ = 146.4 Hz, PPh_2).

L_2 = dppe n = 1, x = 0 (**7a**). Yield: 384 mg (91%). HRMS (ESI): *m*/*z* Calcd. for $[C_{45}H_{41}P_3RhS]^+$: 809.1191; found for $[M-Cl]^+$: 809.1191. ^1H NMR (400 MHz, CD_2Cl_2): δ 1.81–1.93/2.02–2.15 (m/m, 2H/2H, Ph$_2$PCH_2CH_2PPh$_2$), 3.81 (d, $^2J(^{31}P,^1H)$ = 4.4 Hz, 2H, CH_2SPh), 7.06–7.96 (m, 35H, H_{Ph}). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 25.8–26.3/34.7–35.2 (m/m, Ph$_2$PCH_2CH_2PPh$_2$), 32.0 (d, $^1J(^{31}P,^{13}C)$ = 13.7 Hz, CH_2SPh), 125.5–138.1 (C_{Ph}). ^{31}P NMR (81 MHz, THF-d_8): δ 24.4 (ddd, $^2J(^{31}P,^{31}P)$ = 355.0 Hz, $^2J(^{31}P,^{31}P)$ = 35.8 Hz, $^1J(^{103}Rh,^{31}P)$ = 132.2 Hz, PPh_2), 59.0 (ddd, $^2J(^{31}P,^{31}P)$ = 355.0 Hz, $^2J(^{31}P,^{31}P)$ = 33.4 Hz, $^1J(^{103}Rh,^{31}P)$ = 140.9 Hz, *P* of dppe *trans* to *P*), 73.9 (d′t′, $^2J(^{31}P,^{31}P)$ = 35.8 Hz, $^2J(^{31}P,^{31}P)$ = 33.4 Hz, $^1J(^{103}Rh,^{31}P)$ = 183.8 Hz, *P* of dppe *trans* to *Cl*).

L_2 = dppe n = 1, x = 1 (**7b**). Yield: 379 mg (88%). HRMS (ESI): *m*/*z* Calcd. for $[C_{45}H_{41}OP_3RhS]^+$: 825.1141; found for $[M-Cl]^+$: 825.1140. ^1H NMR (400 MHz, CD_2Cl_2): δ 1.70–1.84/1.98–2.24 (m/m, 2H/2H, Ph$_2$PCH_2CH_2PPh$_2$), 3.68/4.39 (dd/dd, $^2J(^{31}P,^1H)$ = 7.4/6.4 Hz, $^2J(^1H,^1H)$ = 13.3/13.3 Hz, 1H/1H, CH_2SOPh), 6.75–8.11 (m, 35H, H_{Ph}). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 26.4–26.8/35.3–35.8 (m/m,

$Ph_2PCH_2CH_2PPh_2$), 63.1 (d, $^1J(^{31}P, ^{13}C) = 13.8$ Hz, CH_2SPh), 124.3–148.2 (C_{Ph}). ^{31}P NMR (81 MHz, CD_2Cl_2): δ 27.9 (ddd, $^2J(^{31}P, ^{31}P) = 353.4$ Hz, $^2J(^{31}P, ^{31}P) = 35.4$ Hz, $^1J(^{103}Rh, ^{31}P) = 142.3$ Hz, PPh_2), 57.9 (ddd, $^2J(^{31}P, ^{31}P) = 353.4$ Hz, $^2J(^{31}P, ^{31}P) = 33.6$ Hz, $^1J(^{103}Rh, ^{31}P) = 142.1$ Hz, *P* of dppe *trans* to *P*), 75.3 (d′t′, $^2J(^{31}P, ^{31}P) = 35.4$ Hz, $^2J(^{31}P, ^{31}P) = 33.6$ Hz, $^1J(^{103}Rh, ^{31}P) = 183.1$ Hz, *P* of dppe *trans* to *Cl*).

L_2 = dppe $n = 1, x = 2$ (**7c**). Yield: 351 mg (80%). HRMS (ESI): *m*/*z* Calcd. for $[C_{45}H_{41}O_2P_3RhS]^+$: 841.1088; found for $[M-Cl]^+$: 841.1092. ^1H NMR (400 MHz, CD_2Cl_2): δ 1.80–1.92/2.04–2.16 (m/m, 2H/2H, $Ph_2PCH_2CH_2PPh_2$), 4.66 (d, $^2J(^{31}P, ^1H) = 4.6$ Hz, 2H, CH_2SO_2Ph), 7.05–7.99 (m, 35H, H_{Ph}). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 25.8–26.2/34.9–35.4 (m/m, $Ph_2PCH_2CH_2PPh_2$), 53.7 (d, $^1J(^{31}P, ^{13}C) = 6.9$ Hz, CH_2SO_2Ph), 125.5–138.1 (C_{Phr}). ^{31}P NMR (81 MHz, CD_2Cl_2): δ 22.0 (ddd, $^2J(^{31}P, ^{31}P) = 361.8$ Hz, $^2J(^{31}P, ^{31}P) = 35.3$ Hz, $^1J(^{103}Rh, ^{31}P) = 135.0$ Hz, PPh_2), 60.5 (ddd, $^2J(^{31}P, ^{31}P) = 361.8$ Hz, $^2J(^{31}P, ^{31}P) = 34.0$ Hz, $^1J(^{103}Rh, ^{31}P) = 142.4$ Hz, *P* of dppe *trans* to *P*), 73.5 (d′t′, $^2J(^{31}P, ^{31}P) = 35.3$ Hz, $^2J(^{31}P, ^{31}P) = 34.0$ Hz, $^1J(^{103}Rh, ^{31}P) = 183.7$ Hz, *P* of dppe *trans* to *Cl*).

L_2 = dppe $n = 2, x = 0$ (**9a**). Yield: 352 mg (82%). HRMS (ESI): *m*/*z* Calcd. for $[C_{46}H_{43}P_3RhS]^+$: 823.1349; found for $[M-Cl]^+$: 823.1364. ^1H NMR (400 MHz, CD_2Cl_2): δ 2.11–2.32 (m, 4H, $Ph_2PCH_2CH_2PPh_2$), 2.40–2.44 (m, 2H, CH_2PPh_2), 2.73–2.82 (m, 2H, CH_2SPh), 7.03–7.49 (m, 35H, H_{Ph}). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 26.2–27.1/30.5–31.6 (m/m, $Ph_2PCH_2CH_2PPh_2$), 32.4 (d, $^1J(^{31}P, ^{13}C) = 22.8$ Hz, CH_2PPh_2), 38.4 (d, $^2J(^{31}P, ^{13}C) = 9.0$ Hz, CH_2SPh), 128.4–134.2 (C_{Ph}). ^{31}P NMR (81 MHz, CD_2Cl_2): δ 58.2 (m, $^2J(^{31}P, ^{31}P) = 284.7$ Hz, $^2J(^{31}P, ^{31}P) = 31.3$ Hz, $^1J(^{103}Rh, ^{31}P) = 131.5$ Hz, *P* of dppe *trans* to *P*), 60.6 (m, $^2J(^{31}P, ^{31}P) = 284.7$ Hz, $^2J(^{31}P, ^{31}P) = 32.1$ Hz, $^1J(^{103}Rh, ^{31}P) = 134.9$ Hz, PPh_2), 65.2 (d′t′, $^2J(^{31}P, ^{31}P) = 31.3$ Hz, $^2J(^{31}P, ^{31}P) = 32.1$ Hz, $^1J(^{103}Rh, ^{31}P) = 161.4$ Hz, *P* of dppe *trans* to *Cl*).

L_2 = dppe $n = 2, x = 1$ (**9b**). Yield: 357 mg (85%). HRMS (ESI): *m*/*z* Calcd. for $[C_{46}H_{43}OP_3RhS]^+$: 839.1297; found for $[M-Cl]^+$: 839.1305. ^1H NMR (400 MHz, THF-d_8): δ 1.82–2.12 (m, 4H, $Ph_2PCH_2CH_2PPh_2$), 2.38–2.46/2.74–2.82 (m/m, 1H/1H, CH_2PPh_2), 2.90–2.98/3.51–3.58 (m/m, 1H/1H, CH_2SOPh), 6.88–8.18 (m, 35H, H_{Ph}). ^{13}C NMR (125 MHz, THF-d_8): δ 20.4 (d, $^1J(^{31}P, ^{13}C) = 21.6$ Hz, CH_2PPh_2), 25.2–26.8/33.5–34.6 (m/m, $Ph_2PCH_2CH_2PPh_2$), 53.6 (d, $^2J(^{31}P, ^{13}C) = 6.3$ Hz, CH_2SOPh), 133.9–145.5 (C_{Ph}). ^{31}P NMR (202 MHz, THF-d_8): δ 23.1 (m, $^2J(^{31}P, ^{31}P) = 328.6$ Hz, $^2J(^{31}P, ^{31}P) = 9.0$ Hz, $^1J(^{103}Rh, ^{31}P) = 133.2$ Hz, PPh_2), 57.0 (m, $^2J(^{31}P, ^{31}P) = 328.6$ Hz, $^2J(^{31}P, ^{31}P) = 48.8$ Hz, $^1J(^{103}Rh, ^{31}P) = 140.9$ Hz, *P* of dppe *trans* to *P*), 74.0 (m, $^2J(^{31}P, ^{31}P) = 9.0$ Hz, $^2J(^{31}P, ^{31}P) = 48.8$ Hz, $^1J(^{103}Rh, ^{31}P) = 184.3$ Hz, *P* of dppe *trans* to *Cl*).

L_2 = dppe $n = 2, x = 2$ (**9c**). Yield: 387 mg (87%). HRMS (ESI): *m*/*z* Calcd. for $[C_{46}H_{43}O_2P_3RhS]^+$: 855.1246; found for $[M-Cl]^+$: 855.1263. ^1H NMR (400 MHz, CD_2Cl_2): δ 1.80–1.90/2.00–2.10 (m/m, 2H/2H, $Ph_2PCH_2CH_2PPh_2$), 2.48–2.53 (m, 2H, CH_2PPh_2), 3.41–3.46 (m, 2H, CH_2SO_2Ph), 7.07–7.93 (m, 35H, H_{Ph}). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 21.2 (d, $^1J(^{31}P, ^{13}C) = 19.6$ Hz, CH_2PPh_2), 25.5–25.9/34.6–35.1 (m/m, $Ph_2PCH_2CH_2PPh_2$), 52.7 (d, $^2J(^{31}P, ^{13}C) = 5.1$ Hz, CH_2SO_2Ph), 127.7–138.7 (C_{Ph}). ^{31}P NMR (202 MHz, CD_2Cl_2): δ 22.1 (ddd, $^2J(^{31}P, ^{31}P) = 357.6$ Hz, $^2J(^{31}P, ^{31}P) = 35.7$ Hz, $^1J(^{103}Rh, ^{31}P) = 133.8$ Hz, PPh_2), 58.9 (ddd, $^2J(^{31}P, ^{31}P) = 357.6$ Hz, $^2J(^{31}P, ^{31}P) = 33.6$ Hz, $^1J(^{103}Rh, ^{31}P) = 140.6$ Hz, *P* of dppe *trans* to *P*), 74.0 (d′t′, $^2J(^{31}P, ^{31}P) = 35.7$ Hz, $^2J(^{31}P, ^{31}P) = 33.6$ Hz, $^1J(^{103}Rh, ^{31}P) = 183.1$ Hz, *P* of dppe *trans* to *Cl*).

L_2 = dppe $n = 3, x = 1$ (**11b**). Yield: 351 mg (79%). HRMS (ESI): *m*/*z* Calcd. for $[C_{47}H_{45}OP_3RhS]^+$: 853.1454; found for $[M-Cl]^+$: 853.1474. ^1H NMR (400 MHz, CD_2Cl_2): δ 1.81–2.36 (m, 8H, $CH_2CH_2CH_2PPh_2 + Ph_2PCH_2CH_2PPh_2$), 2.70–2.77/2.82–2.89 (m/m, 1H/1H, CH_2SOPh), 7.07–7.95 (m, 35H, H_{Ph}). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 19.6 (d, $^2J(^{31}P, ^{13}C) = 4.5$ Hz, $CH_2CH_2CH_2$), 25.8–26.1/34.7–35.3 (m/m, $Ph_2PCH_2CH_2PPh_2$), 27.1 (d, $^1J(^{31}P, ^{13}C) = 21.9$ Hz, CH_2PPh_2), 58.7 (d, $^3J(^{31}P, ^{13}C) = 13.0$ Hz, CH_2SOPh), 123.9–144.7 (C_{Ph}). ^{31}P NMR (81 MHz, CD_2Cl_2): δ 24.2 (ddd, $^2J(^{31}P, ^{31}P) = 351.2$ Hz, $^2J(^{31}P, ^{31}P) = 35.7$ Hz, $^1J(^{103}Rh, ^{31}P) = 131.5$ Hz, PPh_2), 58.9 (ddd, $^2J(^{31}P, ^{31}P) = 351.2$ Hz, $^2J(^{31}P, ^{31}P) = 33.4$ Hz, $^1J(^{103}Rh, ^{31}P) = 140.2$ Hz, *P* of dppe *trans* to *P*), 73.9 (d′t′, $^2J(^{31}P, ^{31}P) = 35.7$ Hz, $^2J(^{31}P, ^{31}P) = 33.4$ Hz, $^1J(^{103}Rh, ^{31}P) = 184.9$ Hz, *P* of dppe *trans* to *Cl*).

3.3. Preparation of $[Rh_3(\mu\text{-}Cl)(\mu\text{-}Ph_2PCH_2SPh\text{-}\kappa P{:}\kappa S)_4][BF_4]_2\cdot 4THF$ (**12**·4THF)

At room temperature to a stirred solution of $[(Rh(cod))_2(\mu\text{-}Cl)_2]$ (123.3 mg, 0.25 mmol) in THF (5 mL) Ph_2PCH_2SPh (154.2 mg, 0.50 mmol) dissolved in THF (2 mL) was added and the mixture was stirred for 1 h. Then, at −78 °C $Ag[BF_4]$ (97.3 mg, 0.50 mmol) dissolved in THF (2 mL) was added. The reaction mixture was slowly warmed to room temperature, stirred for 15 min and the precipitated AgCl was filtered off. After 24 h the microcrystals precipitated were filtered off, washed with THF (3 × 3 mL) and dried in vacuo.

Yield: 82 mg (32%). HRMS (ESI): *m*/*z* Calcd. for $[C_{76}H_{68}ClP_4Rh_2S_4]^+$: 1473.0947; found for $[M-Rh]^+$: 1473.0938. ^1H NMR (400 MHz, CD_2Cl_2): δ 1.82 (m, 16H, THF), 2.78 (s, br, 8H, CH_2SPh), 3.67 (m, 16H, THF), 6.99–8.00 (m, 60H, H_{Ph}). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 25.9 (s, THF), 31.6/42.5 (d/d, $^1J(^{31}P, ^{13}C) = 27.8/26.7$ Hz), 68.0 (s, THF), 128.6–135.8 (C_{Ph}). ^{31}P NMR (81 MHz, CD_2Cl_2): δ 28.4 (ddd, $^2J(^{31}P, ^{31}P) = 35.3$ Hz, $^1J(^{103}Rh, ^{31}P) = 140.7$ Hz, $^2J(^{103}Rh, ^{31}P) = 2.5$ Hz, PPh_2 *trans* to *S*), 45.1 (ddd, $^2J(^{31}P, ^{31}P) = 35.3$ Hz, $^1J(^{103}Rh, ^{31}P) = 180.3$ Hz, $^2J(^{103}Rh, ^{31}P) = 3.5$ Hz, PPh_2 *trans* to *Cl*).

3.4. Preparation of $[Rh\{Ph_2P(CH_2)_nS(O)_xPh\text{-}\kappa P,\kappa S/O\}L_2][BF_4]$ (**13**–**18**)

At room temperature to $[(RhL_2)_2(\mu\text{-}Cl)_2]$ (L_2 = cod, **4**; dppe, **5**; 0.25 mmol) in THF (5 mL) $Ph_2P(CH_2)_nS(O)_xPh$ (0.50 mmol) dissolved in THF (2 mL) was added with stirring. After 1 h $Ag[BF_4]$ (97.3 mg, 0.50 mmol) dissolved in THF (2 mL) was added at −78 °C. The reaction mixture was allowed to warm to room temperature and stirred for 15 min. Then, the precipitated AgCl was filtered off and the filtrate was concentrated under reduced pressure to half of its volume before *n*-pentane (5 mL) was added. The resulted precipitate was filtered off, washed with *n*-pentane (3 × 5 mL) and dried in vacuo.

L_2 = cod, $n = 1, x = 0$ (**13a**). Yield: 234 mg (90%). HRMS (ESI): *m*/*z* Calcd. for $[C_{27}H_{29}PRhS]^+$: 519.0777; found for $[M]^+$: 519.0772. ^1H NMR (200 MHz, CD_2Cl_2): δ 2.26/2.53 (m/m, 3H/5H, 4× CH_2, cod), 5.68/5.33 (s/s, br/br, 2H/2H, 4× *CH*, cod), 5.24 (d, $^2J(^{31}P, ^1H) = 5.8$ Hz, CH_2SPh), 7.25–7.91 (m, 15H, H_{Ph}). ^{13}C NMR (50 MHz, CD_2Cl_2): δ 29.1/31.7 (s/s, br/br, 4× CH_2, cod), 86.5/106.0 (d/s, −/br, $^1J(^{103}Rh, ^{13}C) = 9.3$ Hz, 4× *C*H, cod), 107.7 (d, $^1J(^{13}C, ^{31}P) = 7.3$ Hz, CH_2SPh), 127.5–134.3 (C_{Ph}). ^{31}P NMR (81 MHz, CD_2Cl_2): δ −31.1 (d, $^1J(^{103}Rh, ^{31}P) = 119.5$ Hz, PPh_2).

L_2 = cod, $n = 1, x = 1$ (**13b**). Yield: 274 mg (88%). HRMS (ESI): *m*/*z* Calcd. for $[C_{27}H_{29}OPRhS]^+$: 535.0722; found for $[M]^+$: 535.0718. ^1H NMR (400 MHz, CD_2Cl_2): δ 2.04–2.40/2.49–2.67 (m/m, 5H/3H, 4× CH_2, cod), 3.26/3.69/5.71/5.78 (s/s/s/s, br/br/br/br, 1H/1H/1H/1H, 4× *CH*, cod), 4.23/4.48 (dd/dd, $^2J(^{31}P, ^1H) = 9.0/2.8$ Hz, $^2J(^1H, ^1H) = 14.9/14.9$ Hz, 1H/1H, CH_2SOPh), 7.23–7.60 (m, 15H, H_{Ph}). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 27.8/27.9/32.3/33.1 (s/s/s/s, 4× CH_2, cod), 57.4 (d, $^1J(^{13}C, ^{31}P) = 10.2$ Hz, CH_2SOPh), 69.4/74.1/108.1/109.9 (d/d/dd/dd, br/br, $^1J(^{103}Rh, ^{13}C) = 13.9/14.5/10.5/9.9$ Hz, $^2J(^{31}P_{trans}, ^{13}C) = 7.1/7.2$ Hz, 4× *C*H, cod), 124.1–136.1 (C_{Ph}). ^{31}P NMR (81 MHz, CD_2Cl_2): δ 53.6 (d, $^1J(^{103}Rh, ^{31}P) = 162.7$ Hz, PPh_2).

L_2 = cod, $n = 1, x = 2$ (**13c**). Yield: 268 mg (84%). HRMS (ESI): *m*/*z* Calcd. for $[C_{27}H_{29}O_2PRhS]^+$: 551.0675; found for $[M]^+$: 551.0675. ^1H NMR (400 MHz, CD_2Cl_2): δ 2.08–2.21/2.45–2.59 (m/m, 3H/5H, 4× CH_2, cod), 3.74/5.71 (s/s, br/br, 2H/2H, 4× *CH*, cod), 4.36 (d, $^2J(^{31}P, ^1H) = 8.1$ Hz, CH_2SO_2Ph), 7.51–8.31 (m, 15H, H_{Ph}). ^{13}C NMR

(100 MHz, CD_2Cl_2): δ 27.7/32.7 (s/s, br/br, 4× *C*H_2, cod), 57.2 (d, ^1J(^{13}C, ^{31}P) = 10.0 Hz, *C*H_2SO_2Ph), 72.4/109.6 (d/s, −/br ^1J(^{103}Rh, ^{13}C) = 14.3 Hz, 4× *C*H, cod), 126.0–137.0 (C_{Ph}). ^{31}P NMR (81 MHz, CD_2Cl_2): δ 25.3 (d, ^1J(^{103}Rh, ^{31}P) = 149.0 Hz, *P*Ph_2).

L_2 = cod, *n* = 2, *x* = 0 (**15a**). Yield: 267 mg (86%). HRMS (ESI): *m*/*z* Calcd. for $[C_{28}H_{31}PRhS]^+$: 533.4901; found for $[M]^+$: 533.4909. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 2.30–2.48 (m, 8H, 4× *C*H_2, cod), 2.60–2.65 (m, 2H, *C*H_2PPh$_2$), 2.90–2.99 (m, 2H, *C*H_2SPh), 4.27/5.16 (s/s, br/br, 2H/2H, 4× *C*H, cod), 7.53–7.72 (m, 15H, H_{Ph}). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 29.1/32.0 (s/s, br/br, 4× *C*H_2, cod), 30.2 (d, ^1J(^{31}P, ^{13}C) = 30.2 Hz, *C*H_2PPh$_2$), 37.5 (d, ^2J(^{31}P, ^{13}C) = 7.2 Hz, *C*H_2SPh), 87.7/105.4 (d/dd, ^1J(^{103}Rh, ^{13}C) = 10.8/9.2 Hz, ^2J($^{31}P_{trans}$, ^{13}C) = 6.7 Hz, 4× *C*H, cod), 128.5–133.4 (C_{Ph}). ^{31}P NMR (81 MHz, CD_2Cl_2): δ 59.0 (d, ^1J(^{103}Rh, ^{31}P) = 147.2 Hz, *P*Ph_2).

L_2 = cod, *n* = 2, *x* = 1 (**15b**). Yield: 280 mg (88%). HRMS (ESI): *m*/*z* Calcd. for $[C_{28}H_{31}OPRhS]^+$: 549.4890; found for $[M]^+$: 549.4887. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.77–2.49 (m, 8H, 4× *C*H_2 (cod)), 2.81–3.29 (m, 4H, *C*H_2*C*H_2SOPh), 4.09/4.212/4.24 (s/s/s, br, 1H/2H/1H, 4× *C*H (cod)), 7.27–8.00 (m, 15H, H_{Ph}). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 29.1/32.0 (s/s, br/br, 4× *C*H_2 (cod)), 30.2 (d, ^1J(^{31}P, ^{13}C) = 30.2 Hz, *C*H_2PPh$_2$), 52.9 (s, *C*H_2SOPh), 78.0/78.3/79.0 (d/d/m, ^1J(^{103}Rh, ^{13}C) = 8.1/11.3 Hz, 4× *C*H, cod), 124.6–134.1 (C_{Ph}). ^{31}P NMR (81 MHz, CD_2Cl_2): δ 52.7 (d, ^1J(^{103}Rh, ^{31}P) = 135.8 Hz, *P*Ph_2).

L_2 = cod, *n* = 2, *x* = 2 (**15c**). Yield: 261 mg (80%). HRMS (ESI): *m*/*z* Calcd. for $[C_{28}H_{31}O_2PRhS]^+$: 565.4881; found for $[M]^+$: 565.4875. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 2.01/2.12/2.46–2.62 (m/m/m, 2H/2H/4H, 4× *C*H_2, cod), 3.10–3.15 (m, 2H, *C*H_2PPh$_2$), 3.39–3.46 (m, *C*H_2SO_2Ph), 3.25/5.38 (s/s, br/br, 2H/2H, 4× *C*H, cod), 7.54–7.89 (m, 15H, H_{Ph}). ^{13}C NMR (125 MHz, CD_2Cl_2): δ 20.1 (d, ^1J(^{31}P, ^{13}C) = 23.3 Hz, *C*H_2PPh$_2$), 28.4/31.1/31.3 (s/s/s, −/−/br, 4× *C*H_2, cod), 51.9 (s, *C*H_2SO_2Ph), 71.1/110.4 (d/dd, ^1J(^{103}Rh, ^{13}C) = 15.6/10.1 Hz, ^2J($^{31}P_{trans}$, ^{13}C) = 6.7 Hz, 4× *C*H, cod), 127.6–135.8 (C_{Ph}). ^{31}P NMR (202 MHz, CD_2Cl_2): δ 18.9 (d, ^1J(^{103}Rh, ^{31}P) = 149.5 Hz, *P*Ph_2).

L = cod, *n* = 3, *x* = 0 (**17a**). Yield: 285 mg (90%). HRMS (ESI): *m*/*z* Calcd. for $[C_{29}H_{33}PRhS]^+$: 547.5166; found for $[M]^+$: 547.5168. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 2.02–2.21/2.34–2.42 (m/m, 6H/4H, CH_2*C*H_2CH_2/4× *C*H_2, cod), 2.78 (m, 2H, *C*H_2PPh$_2$), 3.52 (m, 2H, *C*H_2SPh), 3.82/4.64 (s/s, br/br, 2H/2H, 4× *C*H, cod), 7.15–7.61 (m, 15H, H_{Ar}). ^{13}C NMR (125 MHz, CD_2Cl_2): δ 22.7 (s, br, CH_2*C*H_2CH_2), 25.6 (d, ^1J(^{13}C, ^{31}P) = 26.3 Hz, *C*H_2PPh$_2$), 29.26/29.27/32.16/32.19 (s/s/s/s, 4× *C*H_2, cod), 39.3 (d, ^3J(^{13}C, ^{31}P) = 3.6 Hz, *C*H_2SPh), 86.0/104.8 (d/dd, ^1J(^{13}C, ^{103}Rh) = 11.2/10.0 Hz, ^2J(^{13}C, $^{31}P_{trans}$) = 7.1 Hz, 4× *C*H, cod), 126.6–134.0 (C_{Ar}). ^{31}P NMR (80 MHz, CD_2Cl_2): 12.4 (d, ^1J(^{31}P, ^{103}Rh) = 140.0 Hz, *P*Ph_2).

L_2 = cod, *n* = 3, *x* = 1 (**17b**). Yield: 288 mg (87%). HRMS (ESI): *m*/*z* Calcd. for $[C_{29}H_{33}OPRhS]^+$: 563.5157; found for $[M]^+$: 563.5165. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 2.02–2.44/2.50–2.61 (m/m, 8H/3H, CH_2*C*HHPPh$_2$, 4× *C*H_2, cod), 3.06 (m, 1H, CH*H*PPh$_2$), 3.18/3.99 (m/m, 1H/1H, *C*H_2SOPh), 4.15/4.37/4.54/5.17 (s/s/s/s, br/br/br/br, 4H, 4× *C*H, cod), 7.47–8.11 (m, 15H, H_{Ph}). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 17.3 (s, br, *C*H_2CH_2PPh$_2$), 24.2 (d, ^1J(^{31}P, ^{13}C) = 24.2 Hz, *C*H_2PPh$_2$), 28.7/30.7/30.9/31.8 (s/s/s/s, 4× *C*H_2 (cod)), 57.7 (d, ^3J(^{31}P, ^{13}C) = 4.8 Hz, *C*H_2SOPh), 94.5/99.0/104.3–104.7 (d/d/m, ^1J(^{103}Rh, ^{13}C) = 10.0/8.4 Hz, 4× *C*H, cod), 125.5–141.3 (C_{Ph}). ^{31}P NMR (81 MHz, CD_2Cl_2): δ 11.0 (d, ^1J(^{103}Rh, ^{31}P) = 140.0 Hz, *P*Ph_2).

L_2 = cod, *n* = 3, *x* = 2 (**17c**). Yield: 277 mg (83%). HRMS (ESI): *m*/*z* Calcd. for $[C_{29}H_{33}O_2PRhS]^+$: 579.5154; found for $[M]^+$: 579.5155. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.74–2.45 (m, 10H, CH_2*C*H_2CH_2, 4× *C*H_2, cod), 2.61 (m, 2H, *C*H_2PPh$_2$), 3.17/5.32 (s/s, br/br, 2H/2H, 4× *C*H (cod)), 3.57 (m, 2H, *C*H_2SO_2Ph), 7.44–7.82 (m, 15H, H_{Ph}). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 17.5 (s, br, CH_2*C*H_2CH_2), 27.4 (d, ^1J(^{13}C, ^{31}P) = 17.3 Hz, *C*H_2PPh$_2$), 28.3/33.2 (s/s, 4× *C*H_2, cod), 57.0 (d, ^3J(^{13}C, ^{31}P) = 3.8 Hz, *C*H_2SO_2Ph), 71.6/108.3 (d/s, −/br, ^1J(^{103}Rh, ^{13}C) = 15.3 Hz, 4× *C*H, cod), 128.2–136.4 (C_{Ph}). ^{31}P NMR (81 MHz, CD_2Cl_2): δ 24.2 (d, ^1J(^{103}Rh, ^{31}P) = 147.8 Hz, *P*Ph_2).

L_2 = dppe, *n* = 1, *x* = 0 (**14a**). Yield: 394 mg (88%). HRMS (ESI): *m*/*z* Calcd. for $[C_{45}H_{41}P_3RhS]^+$: 809.1180; found for $[M]^+$: 809.1181. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 2.20–2.33/2.44–2.57 (m/m, 2H/2H, $Ph_2PCH_2CH_2PPh_2$), 5.58 (d, ^2J(^{31}P, ^{1}H) = 5.7 Hz, 2H, *C*H_2SPh), 6.94–7.93 (m, 35H, H_{Ph}). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 26.8–27.2/30.7–31.2 (m/m, $Ph_2PCH_2CH_2PPh_2$), 60.3 (d, ^1J(^{31}P, ^{13}C) = 19.3 Hz, *C*H_2SPh), 128.7–135.2 (C_{Ph}). ^{31}P NMR (81 MHz, CD_2Cl_2): δ −22.8 (ddd, ^2J(^{31}P, ^{31}P) = 305.2 Hz, ^2J(^{31}P, ^{31}P) = 22.8 Hz, ^1J(^{103}Rh, ^{31}P) = 111.1 Hz, *P*Ph_2), 61.6 (ddd, ^2J(^{31}P, ^{31}P) = 305.2 Hz, ^2J(^{31}P, ^{31}P) = 29.4 Hz, ^1J(^{103}Rh, ^{31}P) = 139.3 Hz, *P* of dppe *trans* to *P*), 69.1 (ddd, ^2J(^{31}P, ^{31}P) = 22.8 Hz, ^2J(^{31}P, ^{31}P) = 29.4 Hz, ^1J(^{103}Rh, ^{31}P) = 166.6 Hz, *P* of dppe *trans* to *S*).

L_2 = dppe, *n* = 1, *x* = 1 (**14b**). Yield: 392 mg (86%). HRMS (ESI): *m*/*z* Calcd. for $[C_{45}H_{41}OP_3RhS]^+$: 825.1136; found for $[M]^+$: 825.1131. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 1.93–2.78 (m, 4H, $Ph_2PCH_2CH_2PPh_2$), 4.39–4.47 (m, 2H, *C*H_2SOPh), 6.76–8.14 (m, 35H, H_{Ph}). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 22.6–23.0/32.4–32.9 (m/m, $Ph_2PCH_2CH_2PPh_2$), 56.6 (s, br, CH_2SOPh), 124.4–137.5 (C_{Ph}). ^{31}P NMR (202 MHz, CD_2Cl_2): δ 55.5 (ddd, ^2J(^{31}P, ^{31}P) = 308.6 Hz, ^2J(^{31}P, ^{31}P) = 31.6 Hz, ^1J(^{103}Rh, ^{31}P) = 146.3 Hz, *P*Ph_2), 58.9 (ddd, ^2J(^{31}P, ^{31}P) = 308.6 Hz, ^2J(^{31}P, ^{31}P) = 34.3 Hz, ^1J(^{103}Rh, ^{31}P) = 143.6 Hz, *P* of dppe *trans* to *P*), 74.0 (d′t′, ^2J(^{31}P, ^{31}P) = 31.6 Hz, ^2J(^{31}P, ^{31}P) = 34.3 Hz, ^1J(^{103}Rh, ^{31}P) = 182.4 Hz, *P* of dppe *trans* to *O*).

L_2 = dppe, *n* = 1, *x* = 2 (**14c**). Yield: 367 mg (79%). HRMS (ESI): *m*/*z* Calcd. for $[C_{45}H_{41}O_2P_3RhS]^+$: 841.1080; found for $[M]^+$: 841.1090. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 2.06–2.14/2.47–2.56 (m/m, 2H/2H, $Ph_2PCH_2CH_2PPh_2$), 4.67 (d, ^2J(^{31}P, ^{1}H) = 6.9 Hz, 2H, *C*H_2SO_2Ph), 7.16–8.03 (m, 35H, H_{Ph}). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 23.9–24.4/33.5–34.2 (m/m, $Ph_2PCH_2CH_2PPh_2$), 56.4 (s, br, *C*H_2SO_2Ph), 126.0–139.7 (C_{Ph}). ^{31}P NMR (202 MHz, CD_2Cl_2): δ 27.1 (ddd, ^2J(^{31}P, ^{31}P) = 307.0 Hz, ^2J(^{31}P, ^{31}P) 29.5 Hz, ^1J(^{103}Rh, ^{31}P) = 129.7 Hz, *P*Ph_2), 60.1 (ddd, ^2J(^{31}P, ^{31}P) = 307.0 Hz, ^2J(^{31}P, ^{31}P) = 34.4 Hz, ^1J(^{103}Rh, ^{31}P) = 145.6 Hz, *P* of dppe *trans* to *P*), 76.2 (d′t′, ^2J(^{31}P, ^{31}P) = 29.5 Hz, ^2J(^{31}P, ^{31}P) = 34.4 Hz, ^1J(^{103}Rh, ^{31}P) = 184.7 Hz, *P* of dppe *trans* to *O*).

L_2 = dppe, *n* = 2, *x* = 0 (**16a**). Yield: 414 mg (91%). HRMS (ESI): *m*/*z* Calcd. for $[C_{46}H_{43}P_3RhS]^+$: 823.1348; found for $[M]^+$: 823.1354. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 2.18–2.28/2.37–2.44 (m/m, 2H/2H, $Ph_2PCH_2CH_2PPh_2$), 2.54–2.58 (m, 2H, *C*H_2PPh$_2$), 2.78–2.83 (m, 2H, *C*H_2SPh), 7.14–7.57 (m, 35H, H_{Ph}). ^{13}C NMR (125 MHz, CD_2Cl_2): δ 27.4–27.8/31.6–32.1 (m/m, $Ph_2PCH_2CH_2PPh_2$), 33.0 (d, ^1J(^{31}P, ^{13}C) = 23.6 Hz, *C*H_2PPh$_2$), 39.2 (d, ^2J(^{31}P, ^{13}C) = 10.9 Hz, *C*H_2SPh), 129.3–134.9 (C_{Ph}). ^{31}P NMR (202 MHz, CD_2Cl_2): δ 59.4 (m, ^2J(^{31}P, ^{31}P) = 285.2 Hz, ^2J(^{31}P, ^{31}P) = 31.6 Hz, ^1J(^{103}Rh, ^{31}P) = 135.3 Hz, *P*Ph_2), 60.6 (m, ^2J(^{31}P, ^{31}P) = 285.2 Hz, ^2J(^{31}P, ^{31}P) = 31.7 Hz, ^1J(^{103}Rh, ^{31}P) = 132.1 Hz, *P* of dppe *trans* to *P*), 65.5 (d′t′, ^2J(^{31}P, ^{31}P) = 31.7 Hz, ^2J(^{31}P, ^{31}P) = 31.6 Hz, ^1J(^{103}Rh, ^{31}P) = 151.2 Hz, *P* of dppe *trans* to *S*).

L_2 = dppe, *n* = 2, *x* = 1 (**16b**). Yield: 361 mg (78%). HRMS (ESI): *m*/*z* Calcd. for $[C_{46}H_{43}OP_3RhS]^+$: 839.1290; found for $[M]^+$: 839.1284. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.89–3.39 (m, 8H, $Ph_2PCH_2CH_2PPh_2$ + CH_2CH_2SOPh), 6.99–8.23 (m, 35H, H_{Ph}). ^{13}C NMR (125 MHz, CD_2Cl_2): δ 21.6 (d, ^1J(^{31}P, ^{13}C) = 21.0 Hz, *C*H_2PPh$_2$), 26.4–27.6/35.1–35.8 (m/m, $Ph_2PCH_2CH_2PPh_2$), 60.3 (d, ^2J(^{31}P, ^{13}C) = 9.5 Hz, *C*H_2SOPh), 124.4–143.4 (C_{Ph}). ^{31}P NMR (202 MHz, CD_2Cl_2): δ 57.8 (m, ^2J(^{31}P, ^{31}P) = 263.2 Hz, ^2J(^{31}P, ^{31}P) = 33.1 Hz, ^1J(^{103}Rh, ^{31}P) = 136.4 Hz, *P*Ph_2), 59.0 (m, ^2J(^{31}P, ^{31}P) = 263.2 Hz, ^2J(^{31}P, ^{31}P) = 29.4 Hz, ^1J(^{103}Rh, ^{31}P) = 133.1 Hz, *P* of dppe *trans* to *P*), 60.1 (m, ^2J(^{31}P, ^{31}P) = 29.4 Hz, ^2J(^{31}P, ^{31}P) = 33.1 Hz, ^1J(^{103}Rh, ^{31}P) = 145.1 Hz, *P* of dppe *trans* to *S*).

L_2 = dppe, *n* = 2, *x* = 2 (**16c**). Yield: 361 mg (78%). HRMS (ESI): *m*/*z* Calcd. for $[C_{46}H_{43}O_2P_3RhS]^+$: 855.1239; found for $[M]^+$: 855.1246. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.98–2.33 (m, 4H, $Ph_2PCH_2CH_2PPh_2$), 2.91 (m, 2H, *C*H_2PPh$_2$), 3.31 (m, 2H, *C*H_2SO_2Ph), 7.05–7.89 (m, 35H, H_{Ph}). ^{13}C NMR (50 MHz, CD_2Cl_2): δ 22.5 (d, ^1J(^{31}P, ^{13}C) = 1.9 Hz, *C*H_2PPh$_2$), 24.5–25.2/34.0–35.4 (m/m, $Ph_2PCH_2CH_2PPh_2$), 52.4 (d, ^2J(^{31}P, ^{13}C) = 6.4 Hz, *C*H_2SO_2Ph), 127.9–135.8 (C_{Ph}). ^{31}P NMR (81 MHz,

CD_2Cl_2): δ 16.5 (ddd, $^2J(^{31}P, ^{31}P)$ = 304.9 Hz, $^2J(^{31}P, ^{31}P)$ = 34.4 Hz, $^1J(^{103}Rh, ^{31}P)$ = 136.6 Hz, *P*Ph_2), 60.5 (ddd, $^2J(^{31}P, ^{31}P)$ = 304.9 Hz, $^2J(^{31}P, ^{31}P)$ = 33.1 Hz, $^1J(^{103}Rh, ^{31}P)$ = 139.0 Hz, *P* of dppe *trans* to *P*), 77.4 (d′t′, $^2J(^{31}P, ^{31}P)$ = 34.4 Hz, $^2J(^{31}P, ^{31}P)$ = 33.1 Hz, $^1J(^{103}Rh, ^{31}P)$ = 204.5 Hz, *P* of dppe *trans* to *O*).

L = dppe, *n* = 3, *x* = 0 (**18a**). Yield: 425 mg (92%). HRMS (ESI): *m*/*z* Calcd. for $[C_{47}H_{45}P_3RhS]^+$: 837.1504; found for $[M]^+$: 837.1493. ^1H NMR (500 MHz, CD_2Cl_2): δ 1.87–2.02/2.04–2.37 (m, 4H, $PH_2PCH_2CH_2PPh_2$), 1.92–2.01 (m, 2H, $CH_2CH_2CH_2$), 2.30 (m, 2H, $Ph_2PCH_2CH_2CH_2$), 2.96 (m, 2H, $PhSCH_2$), 6.80–7.74 (m, 35H, H_{Ar}). ^{13}C NMR (125 MHz, CD_2Cl_2): δ 21.3 (s, $CH_2CH_2CH_2$), 26.4 (dd, $^1J(^{13}C, ^{31}P)$ = 24.7 Hz, $^3J(^{13}C, ^{31}P_{trans})$ = 1.8 Hz, $Ph_2PCH_2CH_2$), 27.7–27.9/32.5–33.1 (m/m, $Ph_2PCH_2CH_2PPh_2$), 35.9 (dd, $^3J(^{13}C, ^{31}P)/^3J(^{13}C, ^{31}P_{trans})$ = 8.8 Hz/3.4 Hz, $PhSCH_2$), 126.1–135.9 (C_{Ar}). ^{31}P NMR (81 MHz, CD_2Cl_2): δ 7.1 (ddd, $^2J(^{31}P, ^{31}P)$ = 33.2 Hz, $^2J(^{31}P, ^{31}P)$ = 287.8 Hz, $^1J(^{31}P, ^{103}Rh)$ = 131.1 Hz, *P*Ph_2), 59.6 (ddd, $^2J(^{31}P, ^{31}P)$ = 31.4 Hz, $^2J(^{31}P, ^{31}P)$ = 287.8 Hz, $^1J(^{31}P, ^{103}Rh)$ = 128.2 Hz, *P* (dppe) *trans* to *P*), 66.4 (ddd, $^2J(^{31}P, ^{31}P)$ = 31.4 Hz, $^2J(^{31}P, ^{31}P)$ = 33.2, $^1J(^{31}P, ^{103}Rh)$ = 160.0 Hz, *P* (dppe) *trans* to *S*).

L_2 = dppe, *n* = 3, *x* = 1 (**18b**). Yield: 423 mg (90%). HRMS (ESI): *m*/*z* Calcd. for $[C_{47}H_{45}P_3ORhS]^+$: 853.1448; found for $[M]^+$: 853.1456. ^1H NMR (400 MHz, CD_2Cl_2): δ 1.71–2.47 (m, 8H, $CH_2CH_2CH_2PPh_2$ + $Ph_2PCH_2CH_2PPh_2$), 3.16–3.20/3.24–3.29 (m/m, 1H/1H, CH_2SOPh), 6.95–8.14 (m, 35H, H_{Ph}). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 18.5 (s, $CH_2CH_2CH_2$), 27.1–27.5/31.4–31.8 (m/m, $Ph_2PCH_2CH_2PPh_2$), 27.3 (d, $^1J(^{31}P, ^{13}C)$ = 25.4 Hz CH_2PPh_2), 58.7 (dd, $^3J(^{13}C, ^{31}P)$ = 7.6 Hz, $^3J(^{13}C, ^{31}P_{trans})$ = 3.3 Hz, CH_2SOPh), 124.2–143.7 (C_{Ph}). ^{31}P NMR (202 MHz, THF-d_8): δ 7.7 (ddd, $^2J(^{31}P, ^{31}P)$ = 38.2 Hz, $^2J(^{31}P, ^{31}P)$ = 257.4 Hz, $^1J(^{31}P, ^{103}Rh)$ = 132.2 Hz, *P*Ph_2), 56.4 (ddd, $^2J(^{31}P, ^{31}P)$ = 29.3 Hz, $^2J(^{31}P, ^{31}P)$ = 257.4 Hz, $^1J(^{31}P, ^{103}Rh)$ = 134.2 Hz, *P* of dppe *trans* to *P*), 60.0 (ddd, $^2J(^{31}P, ^{31}P)$ = 38.2 Hz, $^2J(^{31}P, ^{31}P)$ = 29.3, $^1J(^{31}P, ^{103}Rh)$ = 148.2 Hz, *P* of dppe *trans* to *S*).

L_2 = dppe, *n* = 3, *x* = 2 (**18c**). ^{31}P NMR (81 MHz, THF-d_8): δ 21.2 (ddd, $^2J(^{31}P, ^{31}P)$ = 30.6 Hz, $^2J(^{31}P, ^{31}P)$ = 329.5 Hz, $^1J(^{31}P, ^{103}Rh)$ = 127.0 Hz, *P*Ph_2), 57.3 (ddd, $^2J(^{31}P, ^{31}P)$ = 28.4 Hz, $^2J(^{31}P, ^{31}P)$ = 329.5 Hz, $^1J(^{31}P, ^{103}Rh)$ = 121.6 Hz, *P* of dppe *trans* to *P*), 70.5 (d′t′, $^2J(^{31}P, ^{31}P)$ = 30.6 Hz, $^2J(^{31}P, ^{31}P)$ = 28.4, $^1J(^{31}P, ^{103}Rh)$ = 182.5 Hz, *P* of dppe *trans* to *O*).

3.5. Preparation of [{Rh(μ-$Ph_2PCH(SPh)$-κC:κP)(cod)}$_2$]·THF (**19**·THF)

At room temperature to a stirred solution of $[(Rh(cod))_2(\mu\text{-}Cl)_2]$ (123.3 mg, 0.25 mmol) in THF (5 mL) Ph_2PCH_2SPh (154.2 mg, 0.50 mmol) dissolved in THF (2 mL) was added and the mixture was stirred for 1 h. The solution was reduced to half of its volume and sodium bis(trimethylsilyl)amide (0.50 mmol, 2 M in THF) was added at −78 °C. After 24 h the crystals formed were filtered off, washed with THF (3 × 3 mL) and dried in vacuo.

Yield: 210 mg (81%). Found: C, 62.48; H, 5.35; Calcd. for $C_{58}H_{64}OP_2S_2Rh_2$ (1109.02): C, 62.81; H, 5.82. ^{31}P NMR (81 MHz, THF): δ 20.8 (m, $^1J(^{103}Rh, ^{31}P)$ = 169.6 Hz, $^2J(^{103}Rh, ^{31}P)$ = 4.0 Hz, $^3J(^{31}P, ^{31}P)$ = 147.4 Hz, *P*Ph_2), 20.9 (m, $^1J(^{103}Rh, ^{31}P)$ = 167.3 Hz, $^2J(^{103}Rh, ^{31}P)$ = 1.0 Hz, $^3J(^{31}P, ^{31}P)$ = 147.4 Hz, *P*Ph_2).

3.6. Preparation of [Rh{$Ph_2PCHS(O)_xPh$-κP,κS/O}L_2] (**20**, **21**) and [Rh{CH{S(O)Ph}$CH_2CH_2PPh_2$-κC,κP}L_2] (**22b**, **23b**)

To $[(RhL_2)_2(\mu\text{-}Cl)_2]$ (L_2 = cod, **4**; dppe, **5**; 0.25 mmol) in THF (5 mL) $Ph_2P(CH_2)_nS(O)_xPh$ (0.50 mmol) dissolved in THF (2 mL) was added with stirring. After 30 min the solution was reduced to half of its volume, cooled to −78 °C and sodium bis(trimethylsilyl)amide (0.50 mmol, 2 M in THF) was added. In case of **20** and **21** *n*-pentane (5 mL) was added, the precipitate filtered off, which was washed with *n*-pentane (3 × 1 mL) and dried in vacuo. In case of **22b** and **23b** the reaction mixtures were allowed to warm to room temperature. The precipitated NaCl was filtered off and *n*-pentane (5 mL) was added to the filtrate. The precipitate obtained was filtered off, washed with *n*-pentane (3 × 1 mL) and dried in vacuo.

L_2 = cod, *n* = 1, *x* = 1 (**20b**).[2] HRMS (ESI): *m*/*z* Calcd. for $[C_{27}H_{29}OPRhS]^+$: 535.0726; found for $[M + H]^+$: 535.0733. ^1H NMR (500 MHz, THF-d_8): δ 1.91–2.41 (m, 8H, 4× CH_2, cod), 2.88 (d, $^2J(^{31}P, ^1H)$ = 10.1 Hz, 1H, $CHSOPh$), 3.81/4.08/5.02/5.14 (s/s/s/s, br/br/br/br, 1H/1H/1H/1H, 4× *CH*, cod), 6.98–8.35 (m, 15H, H_{Ph}). ^{13}C NMR (100 MHz, THF-d_8): δ 27.7/30.0/31.9/32.4 (s/s/s/s, 4× CH_2 (cod)), 70.1 (d, $^1J(^{13}C, ^{31}P)$ = 14.3 Hz, *C*HSOPh), 87.0/87.3/99.4/101.4 (d/d/m/m, $^1J(^{103}Rh, ^{13}C)$ = 10.1/9.7 Hz, 4× *C*H, cod), 124.4–140.2 (C_{Ph}). ^{31}P NMR (81 MHz, THF-d_8): δ 32.2 (d, $^1J(^{103}Rh, ^{31}P)$ = 149.6 Hz, *P*Ph_2).

L_2 = cod, *n* = 1, *x* = 2 (**20c**).[2] HRMS (ESI): *m*/*z* Calcd. for $[C_{27}H_{29}O_2PRhS]^+$: 551.0675; found for $[M + H]^+$: 551.0669. ^1H NMR (500 MHz, CD_2Cl_2): δ 1.91–2.54 (m, 8H, 4× CH_2, cod), 2.71 (d, $^2J(^{31}P, ^1H)$ = 12.8 Hz, 1H, $CHSO_2Ph$), 3.39/4.79/4.84 (s/s/s, br/br/br, 2H/1H/1H, 4× *CH*, cod), 6.86–8.44 (m, 15H, H_{Ph}). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 27.6/28.3/31.2/31.7 (s/s/s/s, 4× CH_2, cod), 69.0 (d, $^1J(^{13}C, ^{31}P)$ = 14.7 Hz, *C*HSO_2Ph), 85.5/87.9/97.8/99.2 (d/d/m/m, $^1J(^{103}Rh, ^{13}C)$ = 9.9/9.8 Hz, 4× *C*H, cod), 124.4–140.2 (C_{Ph}). ^{31}P NMR (81 MHz, CD_2Cl_2): δ 26.6 (d, $^1J(^{103}Rh, ^{31}P)$ = 159.1 Hz, *P*Ph_2).

L_2 = dppe, *n* = 1, *x* = 0 (**21a**).[3] ^{31}P NMR (81 MHz, THF): δ 9.4 (ddd, $^2J(^{31}P, ^{31}P)$ = 8.2 Hz, $^2J(^{31}P, ^{31}P)$ = 248.7 Hz, $^1J(^{31}P, ^{103}Rh)$ = 112.3 Hz, *P*Ph_2), 62.0 (ddd, $^2J(^{31}P, ^{31}P)$ = 10.0 Hz, $^2J(^{31}P, ^{31}P)$ = 248.7 Hz, $^1J(^{31}P, ^{103}Rh)$ = 148.9 Hz, *P* of dppe *trans* to *P*), 69.4 (ddd, $^2J(^{31}P, ^{31}P)$ = 8.2 Hz, $^2J(^{31}P, ^{31}P)$ = 10.0, $^1J(^{31}P, ^{103}Rh)$ = 159.1 Hz, *P* of dppe *trans* to *S*).

L_2 = dppe, *n* = 1, *x* = 1 (**21b**).[2] HRMS (ESI): *m*/*z* Calcd. for $[C_{45}H_{41}OP_3RhS]^+$: 825.1147; found for $[M + H]^+$: 825.1141. ^1H NMR (500 MHz, CD_2Cl_2): δ 1.93–2.29 (m, 4H, $Ph_2PCH_2CH_2PPh_2$), 4.12 (s, br, 1H, *C*HSOPh), 6.97–8.05 (m, 35H, H_{Ph}). ^{13}C NMR (125 MHz, CD_2Cl_2): δ 27.5–28.0/30.0–30.4 (m/m, $Ph_2PCH_2CH_2PPh_2$), 66.6 (s, br, *C*HSOPh), 124.2–143.7 (C_{Ph}). ^{31}P NMR (81 MHz, CD_2Cl_2): δ −25.1 (ddd, $^2J(^{31}P, ^{31}P)$ = 29.0 Hz, $^2J(^{31}P, ^{31}P)$ = 276.7 Hz, $^1J(^{31}P, ^{103}Rh)$ = 106.2 Hz, *P*Ph_2), 60.0 (ddd, $^2J(^{31}P, ^{31}P)$ = 30.4 Hz, $^2J(^{31}P, ^{31}P)$ = 276.7 Hz, $^1J(^{31}P, ^{103}Rh)$ = 145.7 Hz, *P* of dppe *trans* to *P*), 67.1 (ddd, $^2J(^{31}P, ^{31}P)$ = 29.0 Hz, $^2J(^{31}P, ^{31}P)$ = 30.4, $^1J(^{31}P, ^{103}Rh)$ = 157.3 Hz, *P* of dppe *trans* to *S*).

L_2 = dppe, *n* = 1, *x* = 2 (**21c**).[2] HRMS (ESI): *m*/*z* Calcd. for $[C_{45}H_{41}O_2P_3RhS]^+$: 841.1090; found for $[M + H]^+$: 841.1089. ^1H NMR (500 MHz, CD_2Cl_2): δ 1.93–2.51 (m, 4H, $Ph_2PCH_2CH_2PPh_2$), 2.78 (s, 1H, *C*HSOPh) 7.11–7.99 (m, 35H, H_{Ph}). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 25.3–25.8/31.5–31.8 (m/m, $Ph_2PCH_2CH_2PPh_2$), 37.4 (s, br, *C*HSO_2Ph), 125.9–149.7 (C_{Ph}). ^{31}P NMR (81 MHz, CD_2Cl_2): δ 8.7 (ddd, $^2J(^{31}P, ^{31}P)$ = 27.1 Hz, $^2J(^{31}P, ^{31}P)$ = 286.7 Hz, $^1J(^{31}P, ^{103}Rh)$ = 116.4 Hz, *P*Ph_2), 60.4 (ddd, $^2J(^{31}P, ^{31}P)$ = 30.4 Hz, $^2J(^{31}P, ^{31}P)$ = 286.7 Hz, $^1J(^{31}P, ^{103}Rh)$ = 158.1 Hz, *P* of dppe *trans* to *P*), 74.1 (d′t′, $^2J(^{31}P, ^{31}P)$ = 27.1 Hz, $^2J(^{31}P, ^{31}P)$ = 30.4, $^1J(^{31}P, ^{103}Rh)$ = 189.0 Hz, *P* of dppe *trans* to *O*).

L_2 = cod, (**22b**). Yield: 209 mg (74%). HRMS (ESI): *m*/*z* Calcd. for $[C_{29}H_{32}NaOPRhS]$: 585.0859; found for $[M + Na]^+$: 585.0856. ^1H NMR (400 MHz, CD_2Cl_2): δ 1.28–3.03 (m, 12H, $CH_2CH_2PPh_2$ + 4× CH_2, cod), 3.45 (s, br, 1H, *C*HSOPh), 3.94/4.05/5.56 (m/m/s, −/−/br, 1H/1H/2H, 4× *CH*, cod), 6.99–8.26 (m, 15H, H_{Ph}). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 20.8 (d, $^2J(^{31}P, ^{13}C)$ = 13.9 Hz, $CH_2CH_2PPh_2$), 34.0 (d, $^1J(^{31}P, ^{13}C)$ = 26.9 Hz, CH_2PPh_2), 28.4/28.9/29.3/32.5 (s/s/s/s, 4× CH_2, cod), 63.0 (dd, $^2J(^{31}P, ^{13}C)$ = 4.9 Hz, $^1J(^{103}Rh, ^{13}C)$ = 28.7 Hz, *C*HSOPh), 81.1/82.7/93.6/100.4 (d/d/dd/dd, $^1J(^{103}Rh, ^{13}C)$ = 8.6/8.2/11.9/9.8 Hz, $^2J(^{31}P_{trans}, ^{13}C)$ = 7.2/7.8 Hz, 4× *C*H (cod)), 124.3–147.4 (C_{Ph}). ^{31}P NMR (81 MHz, THF-d_8): δ 51.6 (d, $^1J(^{103}Rh, ^{31}P)$ = 174.6 Hz, *P*Ph_2).

[2] Includes NaCl which was not separated.

[3] Not isolated in substance; only characterized by ^{31}P NMR spectroscopy.

Table 4
Crystallographic data, data collection parameters and refinement parameters for **15b**, **15c**, **12**·4THF and **19**·THF.

	15b	**15c**	**12**·4THF	**19**·THF
Empirical formula	$C_{28}H_{31}BF_4OPRhS$	$C_{28}H_{31}BF_4O_2PRhS$	$C_{92}H_{100}B_2ClF_8O_4\ P_4Rh_3S_4$	$C_{58}H_{64}OP_2Rh_2S_2$
M_r	636.28	652.28	2039.64	1108.97
Crystal System	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic
Space group	$Pca2_1$	$Pca2_1$	$P2_1/n$	$P2/n$
a/Å	16.738(1)	17.432(3)	20.6888(5)	13.103(2)
b/Å	9.334(1)	9.376(1)	19.4795(4)	10.1480(9)
c/Å	17.413(1)	16.759(2)	23.0532(6)	18.569(2)
β/°			107.593(2)	94.67(1)
V/Å^3	2720.6(4)	2739.0(6)	8856.1(4)	2460.8(5)
Z	4	4	4	2
D_{calc}/g cm^{-1}	1.553	1.582	1.530	1.497
μ(Mo-K$_\alpha$)/mm^{-1}	0.811	0.811	0.817	0.862
F(000)	1296	1328	4168	1144
θ range/°	2.18–25.98	2.34–26.00	2.09–25.00	1.98–25.00
Rfln. collected	20426	9223	45711	11854
Refln. observed [$I > 2\sigma(I)$]	3964	4682	11941	3227
Rfln. independent	5307 (R_{int} = 0.0912)	4935 (R_{int} = 0.0199)	15572 (R_{int} = 0.0477)	4311 (R_{int} = 0.0384)
Data/restraints/ parameters	5307/1/334	4935/1/343	15572/28/1082	4311/5/316
Goodness-of-fit on F^2	0.928	1.052	1.043	0.836
$R1$, $wR2$ [$I > 2\sigma(I)$]	0.0415, 0.0652	0.0260, 0.0693	0.0451, 0.0938	0.0240, 0.0470
$R1$, $wR2$ (all data)	0.0705, 0.0712	0.0277, 0.0700	0.0678, 0.1018	0.0404, 0.0489
Largest diff. peak and hole/e Å^{-3}	0.624 and −0.351	0.380 and −0.497	0.987 and −0.479	0.380 and −0.299

L_2 = dppe, (**23b**). Yield: 324 mg (76%). HRMS (ESI): m/z Calcd. for [$C_{47}H_{45}OP_3RhS$]: 853.7514; found for [M + H]: 853.7511. ^{1}H NMR (500 MHz, THF-d_8): δ 1.12/1.78 (m/m, 1H/1H, CHCH_2CH$_2$PPh$_2$), 1.93/2.13–2.27/2.58–2.66/3.09 (m/m/m/m, 2H/2H/2H/1H, CHCH$_2$CH_2PPh + Ph$_2$PCH_2CH_2PPh$_2$), 6.83–8.29 (m, 35H, H_{Ph}). ^{13}C NMR (50 MHz, THF-d_8): δ 28.6 (s, CHCH$_2$CH$_2$), 28.8–29.0/37.0–37.4 (m/m, Ph$_2$PCH$_2$CH$_2$PPh$_2$), 29.3 (dd, ^1J(^{13}C, ^{31}P) = 15.9 Hz, ^3J(^{13}C, ^{31}P$_{trans}$) = 5.3 Hz, CHCH$_2$CH$_2$), 57.9–59.8 (m, CHSOPh), 123.9–149.6 (C_{Ph}). ^{31}P NMR (81 MHz, THF-d_8): δ 58.0 (m, ^2J(^{31}P, ^{31}P) = 31.1 Hz, ^2J(^{31}P, ^{31}P) = 307.2 Hz, ^1J(^{31}P, ^{103}Rh) = 156.1 Hz, PPh$_2$), 59.1 (m, ^2J(^{31}P, ^{31}P) = 27.2 Hz, ^2J(^{31}P, ^{31}P) = 31.1 Hz, ^1J(^{31}P, ^{103}Rh) = 128.0 Hz, P of dppe *trans* to C), 65.2 (m, ^2J(^{31}P, ^{31}P) = 27.2 Hz, ^2J(^{31}P, ^{31}P) = 307.2, ^1J(^{31}P, ^{103}Rh) = 159.8 Hz, P of dppe *trans* to P).

3.7. X-ray crystallography

Data for X-ray diffraction analyses of single crystals of **15c**, **12**·4THF and **19**·THF were collected on a Stoe-IPDS 2T diffractometer at 200(2) K and of **15b** on a Stoe-IPDS diffractometer at 223 (2) K using Mo-Kα radiation (λ = 0.7103 Å, graphite monochromator). A summary of the crystallographic data, the data collection parameters and the refinement parameters is given in Table 4. Absorption corrections were applied numerically with X-RED32 [62] (T_{min}/T_{max} 0.86/0.96, **12**·4THF; 0.86/0.92, **15b**; 0.92/0.96, **19**·THF). The structures were solved with direct methods using SHELXS-97 [63] and refined using full-matrix least-square routines against F^2 with SHELXL-97 [64]. All non-hydrogen atoms were refined with anisotropic displacement parameters and hydrogen atoms with isotropic ones. H atoms were placed in calculated positions according to the riding model. In complex **12**·4THF a part of one of the Ph$_2$PCH$_2$SPh ligands has been refined disordered over two positions with a site occupancy of 58.8(4)% (C2A, S2A, C23A–C28A) and 41.2(4)% (C2B, S2B, C23B–C28B). The phenyl rings of these disordered units have been refined constraint. In addition, for the refinement of the THF molecules as packing solvents DFIX and DANG restraints have been used, explaining the comparatively large number of restraints. In complex **19**·THF the THF molecule has been refined disordered over two positions with equal occupancy using 5 DFIX restraints.

3.8. Computational details

DFT calculations were carried out by the Gaussian 03 program package [65] using the hybrid functional B3LYP [66]. 6-311++G (3df,3pd) (P, S) and 6-31+G* (O, C, H) basis sets were employed for main group atoms [65,67]. The valence shell of rhodium has been approximated by a split valence basis set too (Def2-TZVPP); for its core orbitals an effective core potential in combination with consideration of relativistic effects has been used [68]. All systems were fully optimized without any symmetry restrictions. The resulting geometries were characterized as equilibrium structures by the analysis of the force constants of normal vibrations. To limit the computational expense, in the case of complexes with the dppe ligand (**21b**$_{calc}$, **21b**′$_{calc}$) 6-31G* basis sets for O, C and H were used only. Then, after characterizing the structures as equilibrium structures by the analysis of the force constants of normal vibrations, in a second step the molecules were re-optimized with a small step-size (IOP(1/8=3)) using the basis sets 6-31+G* for O, C and H as given above.

Appendix A. Supplementary material

Crystallographic data (excluding structure factors) have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 797346 (**15b**), CCDC 797347(**15c**), CCDC 797348 (**12**·4THF), CCDC 797349 (**19**·THF). These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/cgi-bin/catreq.cgi or from the Business & Administration, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK; fax: (+44) 1223 336033; or email: admin@ccdc.cam.ac.uk.

Appendix. Supplementary material

Supplementary data related to this article can be found online at doi:10.1016/j.jorganchem.2010.12.019.

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