Synthesis, characterization and structures of cyclic organorhodium complexes of the type [Rh{CH(SO_2Ph)$CH_2CH_2YR_2$-κ*C*,κ*Y*}L_2] (YR_2 = PPh_2, NMe_2; L_2 = diphosphine, cyclooctadiene)‡†

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Reactions of dinuclear chloridorhodium(I) complexes [(RhL_2)$_2$(μ-Cl)$_2$] (L_2 = P⌒P: $Me_2P(CH_2)_2PMe_2$, dmpe, **7a**; $Ph_2PCH_2PPh_2$, dppm, **7b**; $Ph_2P(CH_2)_2PPh_2$, dppe, **7c**; $Ph_2P(CH_2)_3PPh_2$, dppp, **7d**; L_2 = cycloocta-1,5-diene, cod, **5**) with lithiated γ-phosphino- and γ-aminofunctionalized propyl phenyl sulfones (Li[CH(SO_2Ph)$CH_2CH_2PPh_2$], **2**; Li[CH(SO_2Ph)$CH_2CH_2NMe_2$], **4**) led to the formation of organorhodium inner complexes of the type [Rh{CH(SO_2Ph)$CH_2CH_2PPh_2$-κ*C*,κ*P*}(P⌒P)] (**8a–d**), [Rh{CH(SO_2Ph)$CH_2CH_2NMe_2$-κ*C*,κ*N*}(P⌒P)] (**9a–d**), [Rh{CH(SO_2Ph)$CH_2CH_2PPh_2$-κ*C*,κ*P*}(cod)]·LiCl (**11**·LiCl) and [Rh{CH(SO_2Ph)$CH_2CH_2NMe_2$-κ*C*,κ*N*}(cod)]·LiCl (**12**·LiCl), respectively. Single-crystal X-ray diffraction analysis of **9c**·THF, **11** and **12** exhibited in all three compounds a distorted square planar coordination of the rhodium atoms having bidentately coordinated neutral co-ligands (cod, **11**, **12**; dppe, **9c**) and anionic α-phenylsulfonyl γ-phosphinopropyl (κ*C*,κ*P*; **11**) and γ-aminopropyl ligands (κ*C*,κ*N*; **12**, **9c**), thus being typical organorhodium inner complexes. Furthermore, organorhodium inner complexes of type **8** were obtained in reactions of the dinuclear chloridobridged rhodium complexes [(RhL_2)$_2$(μ-Cl)$_2$] (L_2 = P⌒P, **7a–d**; cod, **5**; $(C_2H_4)_2$, **6**) with the (non-lithiated) γ-phosphinofunctionalized propyl phenyl sulfone $PhSO_2CH_2CH_2CH_2PPh_2$ (**1**) resulting in the formation of complexes having the sulfone κ*P* coordinated ([$RhClL_2$-($Ph_2PCH_2CH_2CH_2SO_2$Ph-κ*P*)] (L_2 = P⌒P, **10a–d**; cod, **13**; $(C_2H_4)_2$, **14**) which were deprotonated (**10a–d**, **13**) at the α-C atom with lithium diisopropyl amide (LDA) in a subsequent reaction. Single-crystal X-ray diffraction analysis of **10c** (P⌒P = dppe) revealed the expected square-planar coordination geometry of Rh. The identities of all rhodium complexes have been unambiguously proved by microanalyses and NMR spectroscopy (^{1}H, ^{13}C, ^{31}P).

1. Introduction

Metallacycles are cyclic compounds having at least one metal–carbon bond where both the carbon and the metal atom are part of a ring system. In general, they are more stable than their open-chain analogues because hydride elimination reactions are hampered for stereoelectronic reasons. Metallacycles play an important role as model compounds for investigations of organometallic elementary steps.[1,2] Furthermore, they are intermediates in transition metal catalyzed reactions such as oxidative coupling reactions,[3,4] activation of C–H bonds[5–8] and olefin metathesis reactions.[9,10] In 1955, Bähr and Müller described the two complexes [$AlEt_2$($CH_2CH_2CH_2CH_2$OEt-κ*C*,κ*O*)] and [$AlEt_2$($CH_2CH_2CH_2NEt_2$-κ*C*,κ*N*)] and introduced the term "organometallic inner complexes" (also named as organometallic intramolecular-coordination compounds) for metallacycles which are characterized by a 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.[11] In 1966 investigations of organotin inner complexes having a coordinated oxygen or nitrogen atom exhibited a very high stability of five-membered metallacycles.[12] Organotransition metal inner complexes were broadly prepared by cyclometallation (especially orthometallation) reactions resulting in five-membered metallacycles in most cases. A prerequisite for such metallations is that the C–H bonds to be activated are brought in close vicinity to the metal centers mostly by pre-coordination of the organic moiety onto a Lewis-basic heteroatom group YR_n.[13] The first report, the synthesis of an *o*-(phenylazo)phenyl nickel complex, dated from 1963.[14]

Generally, such inner complexes are of importance in three types of applications in organic syntheses:[15] the first application is to utilize the ease of synthesis of these compounds and the chelate ring stability. These cyclometallation products are then further used for the synthesis of organic derivatives by manifold reactions such as insertion, substitution or rearrangement – for example carbonylation,[16] alkenylation,[17] acylation[18] or Diels-Alder reactions.[19] If the cyclometallation products are less stable the five-membered ring intermediates easily can react with substrates in substitution reactions which represents the second type of application. Such reactions are regiospecific since

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‡ Dedicated to Professor Uwe Rosenthal on the occasion of his 60th birthday.

they proceed at the metal bound carbon atom and they have been reported on carbonylations,[20] cross-coupling reactions,[21] ring expansions[22] or carbocyclizations.[23] The third kind of application are metal-catalyzed reactions where inner complexes are involved. These reactions include, in organic chemistry widely used, cross-coupling reactions like the Stille, Suzuki or Heck reactions,[24–26] rearrangements,[27] metatheses,[28–30] reductions[31] and other reactions.

We are interested in α-sulfur functionalized propyl ligands having an additional Lewis-basic heteroatom group ($YR_2 = PPh_2$, NMe_2) in γ-position, being favorable for the formation of five-membered MC_3Y cycles. In the case of lithiated γ-functionalized propyl phenyl sulfides of the type [Li{CH(SPh)CH_2-CH_2YR_n}(tmeda)] (YR_n = NMe_2, O*t*-Bu) the formation of organolithium inner complexes by coordination of the YR_n group could be unambiguously proved by single-crystal X-ray diffraction analysis.[32,33] However, lithiated alkyl phenyl sulfones, regardless whether they bear a Lewis-basic heteroatom group YR_n in γ-position or not, are typically dimeric molecules in the solid state having no metal–carbon bonds but "free" α-carbanionic centers[34] and only few examples with a lithium–carbon bond could be structurally characterized.[35–37] Here we report on the formation of five-membered rhodacycles with the general formula [Rh{CH(SO_2Ph)$CH_2CH_2YR_2$-κ*C*,κ*Y*}L_2] ($YR_2 = PPh_2$, NMe_2; L_2 = diphosphine, cyclooctadiene), thus being cyclic organorhodium complexes.

2. Results and discussion

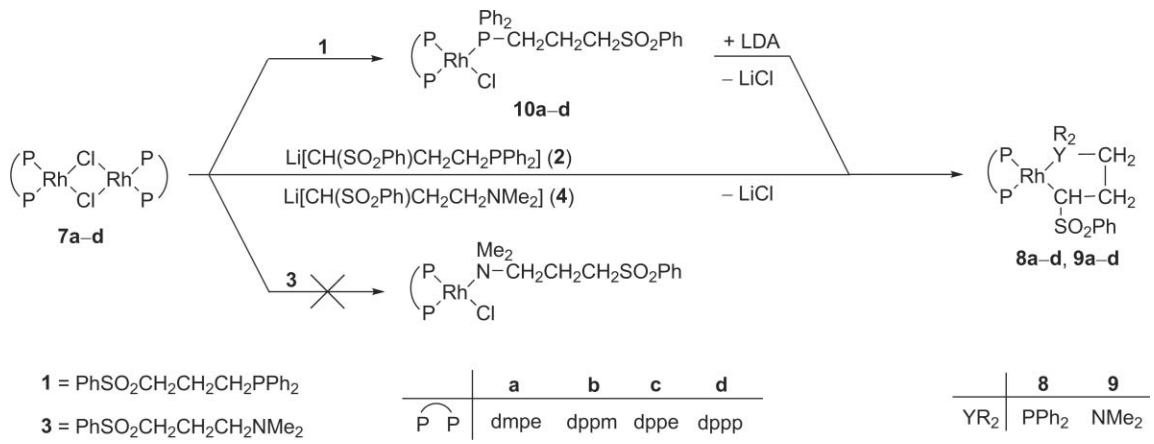
2.1. Synthesis

The reactions of dinuclear diphosphine-chloridorhodium complexes **7a–d** with lithiated γ-phosphino- and γ-aminofunctionalized propyl phenyl sulfones **2** and **4** resulted in the formation of organorhodium inner complexes of the type [Rh{CH(SO_2Ph)-$CH_2CH_2PPh_2$-κ*C*,κ*P*}(P⌒P)] (**8a–d**) and [Rh{CH(SO_2Ph)-$CH_2CH_2NMe_2$-κ*C*,κ*N*}(P⌒P)] (**9a–d**), respectively (Scheme 1). In the sense of one-pot reactions, at first the requisite sulfones $PhSO_2CH_2CH_2CH_2PPh_2$ (**1**) and $PhSO_2CH_2CH_2CH_2NMe_2$ (**3**) were lithiated with *n*-BuLi in toluene followed by the reaction with the rhodium complexes **7a–d** at −78 °C. The same reactions were found to proceed in THF as solvent but difficulties encountered to obtain the complexes free of LiCl in this way. The yellowish to orange air-sensitive complexes **8a–d**/**9a–d** were obtained in yields between 48 and 91%. All complexes were found to decompose in methylene chloride and chloroform at room temperature and, additionally, complex **9d** also in THF.

Another route to obtain the organometallic inner complexes of type **8** were the reactions of the dimeric diphosphine-chloridorhodium complexes **7a–d** with the (non-lithiated) γ-phosphinofunctionalized propyl phenyl sulfone $PhSO_2CH_2CH_2CH_2PPh_2$ (**1**) resulting in the formation of type **10** complexes [RhCl(P⌒P)($Ph_2PCH_2CH_2CH_2SO_2$Ph-κ*P*)] that contain the sulfone in a κ*P* coordination mode (Scheme 1). These chloridorhodium complexes with $PhSO_2CH_2CH_2CH_2PPh_2$-κ*P* ligands were isolated in 65–88% yield and proved to be air-sensitive, too. In contrast to **10a** and **10d**, the complexes **10b** and **10c** were found to be stable in methylene chloride. Type **10** complexes reacted with lithium diisopropylamide (LDA) in toluene/THF under deprotonation neighboured to the sulfur center (α-CH_2 group) of the phosphinofunctionalized sulfone ligand resulting in the formation of the inner complexes **8a–d**. Using MeLi or *n*-BuLi as deprotonating agent led to decomposition which might be caused by the stronger nucleophilic character of these bases. In contrast, the γ-aminofunctionalized sulfone $PhSO_2CH_2CH_2CH_2NMe_2$ (**3**) did not react with type **7** complexes at all (Scheme 1).

As the diphosphine complexes [{Rh(P⌒P)}$_2$(μ-Cl)$_2$] (**7a–d**), the respective cyclooctadiene complex [{Rh(cod)}$_2$(μ-Cl)$_2$] (**5**) was found to react with the lithiated γ-phosphino and γ-aminofunctionalized propyl phenyl sulfones **2** and **4** as well, yielding the organorhodium inner complexes **11** and **12** (Scheme 2). Precipitation from the reaction mixtures (toluene solutions) with *n*-pentane resulted in the formation of the LiCl adducts ([Rh{CH(SO_2Ph)$CH_2CH_2PPh_2$-κ*C*,κ*P*}(cod)]·LiCl, **11**·LiCl; [Rh{CH(SO_2Ph)$CH_2CH_2NMe_2$-κ*C*,κ*N*}(cod)]·LiCl, **12**·LiCl) as yellow powders. Recrystallisation from THF/*n*-pentane and THF, respectively, gave well shaped crystals of complexes **11** and **12** which were shown to be free of LiCl by X-ray diffraction analyses.

The analogous reactions of the ethylene complex [{Rh(C_2H_4)$_2$}$_2$(μ-Cl)$_2$] (**6**) with **2** and **4** led to decomposition. On

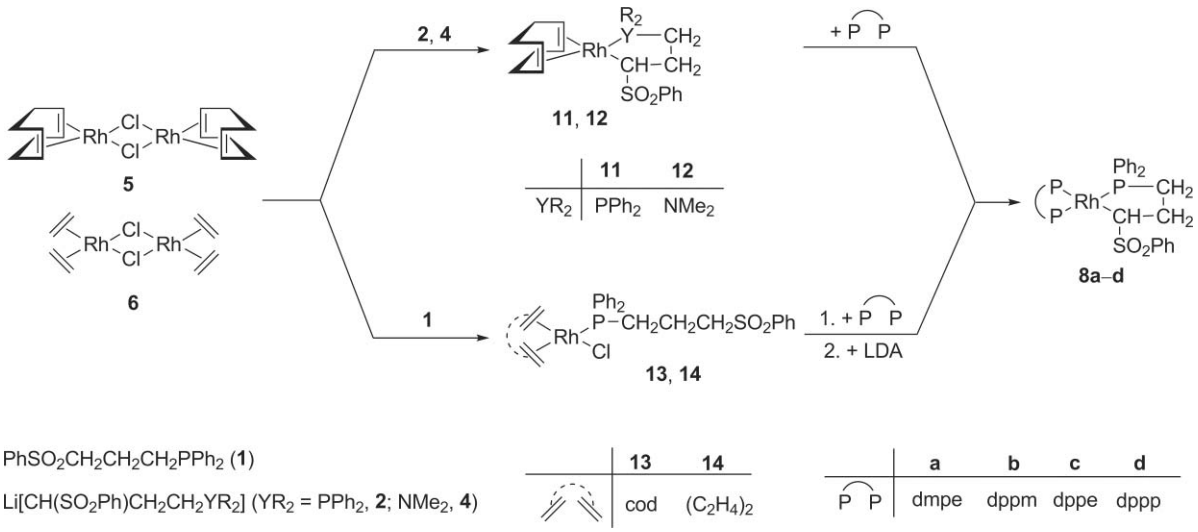


Scheme 1 Synthesis of organorhodium inner complexes **8a–d** and **9a–d**.

Table 1 Selected NMR spectroscopic data (δ in ppm, J in Hz) of [RhClL$_2$(Ph$_2$PCH$_2$CH$_2$CH$_2$SO$_2$Ph-κ*P*)] (**10a–d**, **13**, **14**). The values for PhSO$_2$CH$_2$CH$_2$CH$_2$PPh$_2$ (**1**) are given for comparison

		PhSO$_2$C$_\alpha$H$_2$–C$_\beta$H$_2$–C$_\gamma$H$_2$–PPh$_2$				Co-ligand L$_2$	
	L$_2$	$\delta_{\alpha\text{-C}}$ ($^3J_{P,C}$)	$\delta_{\beta\text{-C}}$ ($^2J_{P,C}$)	$\delta_{\gamma\text{-C}}$ ($^1J_{P,C}$)	δ_P ($^1J_{Rh,P}$)	δ_P ($^1J_{Rh,P}$)[a]	$\delta_{P'}$ ($^1J_{Rh,P'}$)[a]
10a	dmpe	58.2 (10.3)	20.7 (5.2)	27.6 (20.9)	23.7 (133.1)	45.8 (137.7)	43.3 (166.4)
10b	dppm	56.8 (12.7)	19.7 (5.2)	26.3 (22.3)	23.3 (134.2)	–41.5 (118.5)	–15.5 (156.0)
10c	dppe	57.6 (13.6)	20.1 (5.1)	26.9 (22.5)	23.7 (131.6)	58.9 (140.2)	73.9 (184.7)
10d	dppp	58.2 (13.0)	21.3 (7.1)	28.0 (24.0)	25.6 (132.9)	12.9 (132.5)	34.0 (174.9)
13	cod	57.1 (13.8)	20.0 (2.7)	26.6 (25.2)	27.8 (149.2)	—	—
14	$(C_2H_4)_2$	56.7 (14.0)	19.9 (s, br)	27.9 (31.0)	48.7 (186.1)	—	—
1	—	56.7 (13.6)	19.5 (18.8)	26.7 (12.5)	–16.4	—	—

[a] P and P′ are *trans* to P of the PhSO$_2$CH$_2$CH$_2$CH$_2$PPh$_2$ ligand and Cl, respectively.



Scheme 2 Synthesis of organorhodium inner complexes **8a–d**, **11**, **12** and chloridorhodium phosphine complexes **13** and **14**.

the other hand, the olefin complexes **5** and **6** reacted with the non-lithiated γ-phosphinofunctionalized propyl phenyl sulfone **1** yielding the chloridorhodium complexes **13** and **14** with PhSO$_2$CH$_2$CH$_2$CH$_2$PPh$_2$-κ*P* ligands (Scheme 2). As for **7a–d**, neither **5** nor **6** was found to react with the γ-aminofunctionalized propyl phenyl sulfone **3**.

Complexes **11**·LiCl, **12**·LiCl, **13** and **14** were isolated with yields between 66 and 83% as yellow to orange solids. While [RhCl(cod)(Ph$_2$PCH$_2$CH$_2$CH$_2$SO$_2$Ph-κ*P*)] (**13**) was air-stable and stable in chloroform as well as in methylene chloride, the complexes **11**·LiCl, **12**·LiCl and **14** were sensitive against air and moisture and decomposed in halogenated solvents. The identities of all complexes have been confirmed by elemental analyses, NMR (^{1}H, ^{13}C, ^{31}P) spectroscopic investigations and single-crystal X-ray diffraction analyses (**9c**·THF, **10c**, **11**, **12**). Complex **11** could also be obtained by deprotonation of the cyclooctadiene-chloridorhodium complex **13** with LDA. Complexes **11** and **13**/**14** opened up another route for the synthesis of the organorhodium inner complexes **8a–d** *via* ligand substitution (cod by P⁀P) and *via* ligand substitution (cod/C$_2$H$_4$ by P⁀P) followed by reaction with LDA, respectively (Scheme 2). Unexpectedly, addition of diphosphines to the γ-aminofunctionalized propyl inner complex [Rh(cod){CH(SO$_2$Ph)CH$_2$CH$_2$NMe$_2$-κ*C*,κ*N*}] (**12**) did not lead to the formation of the respective inner rhodium complexes **9a–d** but to the predominant formation (> 90%) of the cationic bis(diphosphine)rhodium(I) complexes [Rh(P⁀P)$_2$]$^+$ which have been prepared by an alternative method before.[38,39]

2.2. Spectroscopic characterization

2.2.1. Rhodium complexes with PhSO$_2$CH$_2$CH$_2$CH$_2$PPh$_2$-κ*P* ligands. Selected NMR spectroscopic parameters of the chloridorhodium complexes with PhSO$_2$CH$_2$CH$_2$CH$_2$PPh$_2$-κ*P* ligands (**10a–d**, **13** and **14**) are given in Table 1. The ^{31}P NMR spectra of complexes **10b–d** are of first order with an AEMX spin system (A, E, M = ^{31}P; X = ^{103}Rh) whereas that of **10a** is of higher order (ABMX spin system) which was analyzed by using the PERCH software package.[40] Although in **10a** the ^{13}C atoms of the propyl chain are part of a higher order spin systems, simulations with the PERCH software exhibited that they can be treated as first order. In type **10** complexes the differences in the two $^1J_{Rh,P}$ coupling constants of the P⁀P co-ligand between ΔJ = 12.7 Hz (**10a**) and ΔJ = 44.5 Hz (**10c**) allowed the assignment of the P atoms *trans* to the PhSO$_2$CH$_2$CH$_2$CH$_2$PPh$_2$ ($^1J_{Rh,P}$ = 118.5–141.4 Hz) and *trans* to the chlorido ligand ($^1J_{Rh,P}$ = 154.1–184.7 Hz), respectively, as given in Table 1. The κ*P* coordination of the γ-phosphinopropyl phenyl sulfone ligand is clearly shown by the lowfield shift of the ^{31}P nucleus by about 40 ppm for type **10** complexes. The

Table 2 Selected NMR spectroscopic data (δ in ppm, J in Hz) of organorhodium inner complexes [Rh{CH(SO_2Ph)$CH_2CH_2YR_2$-κC,κY}L_2] (**8a–d**, **9a–d**, **11**, **12**). The values for $PhSO_2CH_2CH_2CH_2PPh_2$ (**1**) and $PhSO_2CH_2CH_2CH_2NMe_2$ (**3**) are given for comparison

		$PhSO_2C_\alpha H–C_\beta H_2–C_\gamma H_2–YR_2$				Co-ligand L_2	
	L_2/YR_2	$\delta_{\alpha\text{-}C}$	$\delta_{\beta\text{-}C}$ ($^2J_{P,C}$)	$\delta_{\gamma\text{-}C}$ ($^1J_{P,C}$)	δ_P ($^1J_{Rh,P}$)	δ_P ($^1J_{Rh,P}$)	$\delta_{P'}$ ($^1J_{Rh,P'}$)
8a	dmpe/PPh_2	61.0–61.8 (m)	30.3 (19.5)	36.5 (22.9)	58.0 (144.3)	35.8 (128.8)[a]	35.5 (144.8)[a]
8b	dppm/PPh_2	61.6–62.6 (m)	28.5 (17.3)	34.2 (23.3)	57.9 (154.8)	13.7 (113.5)[a]	–21.0 (133.7)[a]
8c	dppe/PPh_2	61.1–63.0 (m)	29.5 (24.0)	35.0 (22.2)	55.5 (153.1)	59.3 (133.0)[a]	61.1 (155.5)[a]
8d	dppp/PPh_2	66.1–67.0 (m)	29.5 (14.4)	37.5 (23.8)	55.6 (156.0)	16.3 (127.1)[a]	19.5 (150.1)[a]
9a	dmpe/NMe_2	57.0 (9.1/69.2)[b]	30.6	66.3	—	28.3 (148.2)[c]	47.1 (175.9)[c]
9b	dppm/NMe_2	57.1 (7.0/68.8)[b]	30.4	65.8	—	–17.2 (125.0)[c]	–1.7 (165.5)[c]
9c	dppe/NMe_2	60.9 (7.9/67.9)[b]	30.4	66.3	—	58.2 (150.5)[c]	76.0 (188.1)[c]
9d	dppp/NMe_2	61.4 (8.9/67.0)[b]	29.8	66.4	—	14.2 (141.3)[c]	37.8 (187.8)[c]
11	cod/PPh_2	63.0 (4.6)[d]	29.7 (13.3)	33.0 (26.9)	52.0 (172.0)	—	—
12	cod/NMe_2	54.9	30.6	66.5	—	—	—
1	—	56.7 (13.6)[e]	19.5 (18.8)	26.7 (12.5)	–16.4	—	—
3	—	54.0	20.7	57.2	—	—	—

[a] P and P′ are *trans* to *C* and to *P* of the P⁀CHSO$_2$Ph ligand, respectively. [b] $^2J_{P,C}$ coupling constants to the P atoms (*cis*/*trans*) of the P⁀P co-ligand L_2. [c] P and P′ are *trans* to *C* and to *N* of the $PhSO_2CHCH_2CH_2NMe_2$ ligand, respectively. [d] $^2J_{P,C}$. [e] $^3J_{P,C}$.

$^1J_{Rh,P}$ couplings between 131.6 and 134.2 Hz are typical for phosphorus atoms having another *P* atom in *trans* position.[41–43] The coordination induced shifts of the aliphatic carbon atoms of the $PhSO_2CH_2CH_2CH_2PPh_2$ ligand proved to be small (up to 1.8 ppm) but considerably large for the respective proton shifts (up to 0.68 ppm). The $^1J_{Rh,P}$ couplings in complexes **13** (149.2 Hz) and **14** (186.1 Hz) are as expected for ^{31}P atoms having an olefin ligand in the *trans* position.[44–47] The downfield shift of the ^{31}P nucleus in **14** (δ 48.7 ppm) is even larger than in **10a–d** and **13** (δ 23.3–27.8 ppm) but still in the usual region.[48,49] Compared to [{Rh(cod)}$_2$(μ-Cl)$_2$] (**5**; –CH=CH–: δ_C 78.7 ppm, δ_H 4.18 ppm) and [{Rh(C_2H_4)$_2$}$_2$(μ-Cl)$_2$] (**6**; CH_2=CH_2: δ_C 60.7 ppm, δ_H 3.10 ppm), in the olefin complexes **13** and **14** the olefin carbon atoms and protons are no longer chemically equivalent and were found at δ_C 70.6/105.3 ppm δ_H 2.96/5.40 ppm (**13**) and at δ_C 48.2 (br) ppm δ_H 2.05/2.90 ppm (br/br) (**14**). The broadening of these signals in complex **14** and of the aliphatic protons of the phosphino ligand may indicate molecular dynamics possibly an exchange of the ethylene ligand by solvent molecules (THF).

2.2.2. Organorhodium inner complexes. Selected NMR spectroscopic parameters of the organorhodium inner complexes (**8a–d**, **9a–d**, **11**, **12**) are given in Table 2. The ^{31}P NMR spectra of complexes **8b**, **9a–d** and **11** are of first order with AEMX (A, E, M = ^{31}P; X = ^{103}Rh) (**8b**), AMX (**9a–d**) and AX spin systems (**11**). The ^{31}P nuclei in complexes **8a** and **8d** are part of ABMX spin systems (A, B, M = ^{31}P; X = ^{103}Rh) (Fig. 1) and those of **8c** of an ABCX system (Fig. 2). In complexes **8a–d** the signals of the α-C atoms proved to be of too high multiplicity to be analyzed whereas, as for **10a**, the signals of the β- and γ-C atoms in **8a** and **8d** could be analyzed as first order spectra. For complex **8c** the $^nJ_{P,C}$ coupling constants (n = 1, 2, Table 2) were obtained by simulation the ABCMX spin systems (A, B, C = ^{31}P; M = ^{13}C; X = ^{103}Rh) using the PERCH software. Due to the less multiplicity in complexes **9a–d** all coupling constants were obtained directly from the spectra, among them the $^1J_{Rh,C}$ couplings (25.5–27.1 Hz).

In the organorhodium inner complexes **8a–d** the differences between the two $^1J_{Rh,P}$ coupling constants of the co-ligand P⁀P from ΔJ = 16.0 Hz (**8a**) to ΔJ = 23.0 Hz (**8d**) allowed the assignment of the P atoms *trans* to the P ($^1J_{Rh,P}$ = 133.7–155.5 Hz)

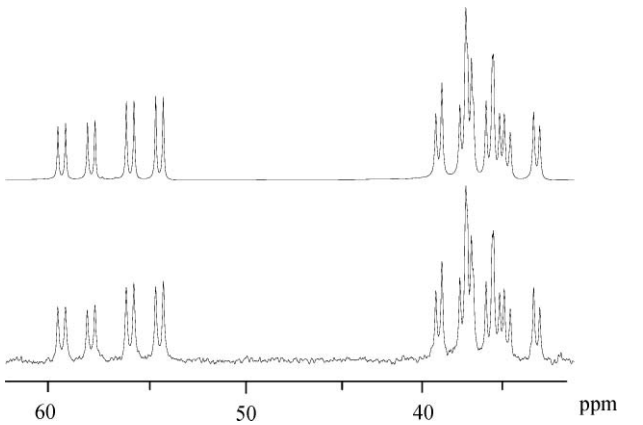


Fig. 1 Simulated (above) and measured (81 MHz, below) ^{31}P NMR spectrum of [Rh{CH(SO_2Ph)$CH_2CH_2PPh_2$-κC,κP}(dmpe)] (**8a**). The ABM part of the ABMX spin system is shown (A, B, M = ^{31}P; X = ^{103}Rh).

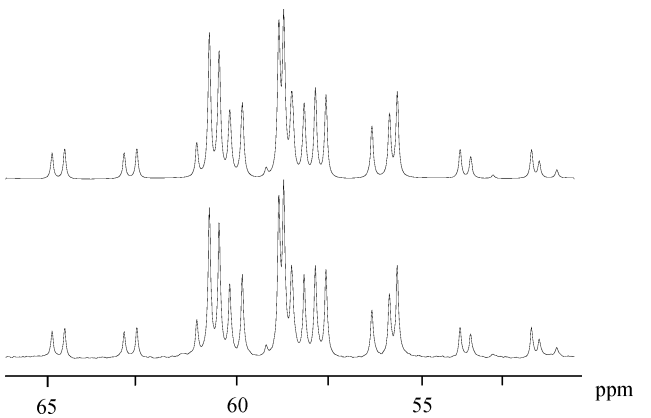


Fig. 2 Simulated (above) and measured (81 MHz, below) ^{31}P NMR spectrum of [Rh{CH(SO_2Ph)$CH_2CH_2PPh_2$-κC,κP}(dppe)] (**8c**). The ABC part of the ABCX (A, B, C = ^{31}P, X = ^{103}Rh) spin system is shown.

and the C atom ($^1J_{Rh,P}$ = 113.5–133.0 Hz) of the P⁀CHSO$_2$Ph ligand, respectively. In complexes **9a–d** the differences between the two $^1J_{Rh,P}$ coupling constants (ΔJ = 27.7–46.5 Hz) are greater due to the smaller *trans* influence of the NMe_2 compared to the

PPh_2 group.[50,51] In the case of complexes **8** these assignments were further confirmed by the magnitudes of the $^2J_{P,P}$ coupling constants: the P atoms of the P⁀P ligands *trans* to C have two *cis*-couplings whereas the P′ atoms (*trans* to P of the P⁀CHSO$_2$Ph ligand) have one *trans*- and one *cis*-coupling. Both, the *cis* ($^2J_{P,P\,cis}$ = 25.8–67.7 Hz) as well as the *trans* coupling constants ($^2J_{P,P\,trans}$ = 310.8–340.5 Hz) are in the expected range[52,53] Deprotonation of **1**/**3** and the κ*C*,κ*P*/κ*C*,κ*N* coordination of the resulting anions to Rh gives rise to lowfield shifts of the α-C atoms by 5–10 ppm and of the P atoms (**8a–d**) by about 70 ppm. The greater *trans* influence of the PPh_2 group in complexes **8a–d** compared to the NMe_2 group in complexes **9a–d** is reflected in markedly smaller (by 31–38 Hz) coupling constants between Rh and the P atom in *trans* position. In the inner complex **11** having a cod co-ligand the $^1J_{Rh,P}$ coupling constant was found to be greater by about 20 Hz compared to **8a–d** reflecting the order of the *trans* influence cod < diphosphines.

2.3. Structural investigations

2.3.1. Structure of [RhCl(dppe)(Ph$_2$PCH$_2$CH$_2$CH$_2$SO$_2$Ph-κ*P*)] (10c). Crystals of **10c** suitable for X-ray diffraction analysis were obtained from THF/*n*-pentane at room temperature. The compound crystallized in isolated monomeric molecules without unusual intermolecular interactions (shortest distance between non-hydrogen atoms: 3.240(5) Å, O2···C46′). The molecular structure is shown in Fig. 3, selected structural parameters are given in the figure caption. The rhodium atom is square-planar coordinated by the two phosphorus atoms of the dppe ligand, by the phosphorus atom of the phosphinofunctionalized sulfone as well as by a chlorido ligand. Due to the bite of the dppe ligand the P1–Rh–P2 angle (85.2(4)°) is slightly diminished. The five-membered rhodacycle (RhP_2C_2) adopts a half-chair conformation, twisted on the two C atoms. The Rh–P3 and Rh–P2 bonds (2.320(1)/2.263(1) Å) are in the expected range for P atoms having another phosphorus atom in *trans* position.[54–56] As expected, the Rh–P1 bond (2.179(1) Å) is shorter than the other two Rh–P bonds due to the smaller *trans* influence of the chlorido ligand.[57–59]

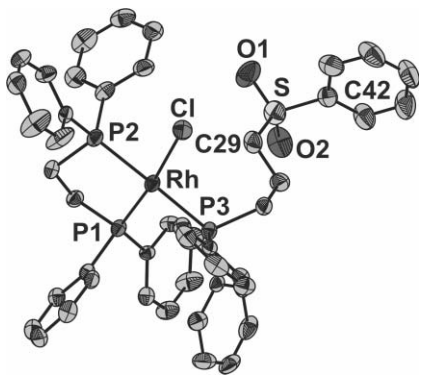


Fig. 3 Molecular structure of [RhCl(dppe)(Ph$_2$PCH$_2$CH$_2$CH$_2$SO$_2$Ph-κ*P*)] in crystals of **10c**. The ellipsoides are shown with a probability of 50%. H atoms have been omitted for clarity. Selected structural parameters (distances in Å, angles in °): Rh–Cl 2.391(1), Rh–P1 2.179(1), Rh–P2 2.263(1), Rh–P3 2.320(1), Cl–Rh–P2 89.0(3), Cl–Rh–P3 89.9(3), P1–Rh–P2 85.2(4), P1–Rh–P3 95.8(3), Cl–Rh–P1 174.1(3), P2–Rh–P3 176.6(4), C29–S–C42 103.9(2), O1–S–O2 118.4(2).

The O1–S–O2 (118.4(2)°) and C29–S–C42 (103.9(2)°) angles were found to be as those in sulfones (median O–S–O: 118.6°, lower/higher quartile: 117.9/119.3° n = 2490; median C–S–C: 105.0°, lower/higher quartile: 103.6/103.4° n = 2490; n–number of observations[60]).

2.3.2. Structures of organorhodium inner complexes. Crystals of [Rh{CH(SO$_2$Ph)CH$_2$CH$_2$NMe$_2$-κ*C*,κ*N*}(dppe)]·THF (**9c**·THF), [Rh{CH(SO$_2$Ph)CH$_2$CH$_2$PPh$_2$-κ*C*,κ*P*}(cod)] (**11**) and [Rh{CH(SO$_2$Ph)CH$_2$CH$_2$NMe$_2$-κ*C*,κ*N*}(cod)] (**12**) suitable for X-ray diffraction analyses were obtained from THF/*n*-pentane (**9c**·THF, **12**) and THF (**11**), respectively, at room temperature. All compounds crystallized in isolated molecules without unusual intermolecular interactions (shortest distance between non-hydrogen atoms: 3.722(7) Å, C19···C4′, **9c**·THF; 3.183(6) Å, O1···C12′, **11**; 3.285(5) Å, C4···C4′, **12**). The molecular structures are shown in Fig. 4–6. Selected structural parameters are given in the figure captions. In all three complexes the rhodium atoms are located in the center of a distorted square planar environment. The primary donor sets of the rhodium atoms are built up by a bidentate neutral ligand (1,5-cyclooctadiene, **11**, **12**; dppe, **9c**·THF) and by a bidentate anionic α-phenylsulfonyl γ-phosphinopropyl (**11**) and γ-aminopropyl ligand (**12**, **9c**·THF) with a κ*C*,κ*P* and a κ*C*,κ*N* coordination, respectively. In all three complexes the five-membered rhodacycles $RhYC_3$ reveal quite small C1–Rh–Y angles (81.3(7)–82.1(1)°) pointing to a relatively small bite of the chelate ligand. While the two nitrogen containing rhodacycles $RhNC_3$ in **9c**·THF and **12** adopt a half-chair configuration twisted on C2 and C3 the metallacycle $RhPC_3$ in **11** adopts an envelope configuration on C3.

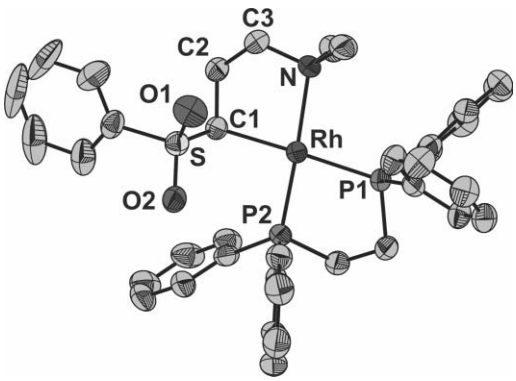


Fig. 4 Molecular structure of [Rh{CH(SO$_2$Ph)CH$_2$CH$_2$NMe$_2$-κ*C*,κ*N*}(dppe)] in crystals of **9c**·THF. The ellipsoides are shown with a probability of 50%. H atoms have been omitted for clarity. Selected structural parameters (distances in Å, angles in °): Rh–P1 2.258(1), Rh–P2 2.191(1), Rh–C1 2.161(4), Rh–N 2.222(4), P1–Rh–P2 83.5(4), P1–Rh–N 99.8(9), P2–Rh–C1 94.1(1), N–Rh–C1 82.1(1), P1–Rh–C1 175.1(1), P2–Rh–N 172.6(1).

Obviously due to the greater size of the *P* atom (compared to the *N* atom) the Rh–C1 bond in **11** is longer (2.181(3) Å) than in complexes **9c**·THF (2.161(4) Å) and **12** (2.149(3) Å). On the other hand, the Rh–P bond in **11** (2.264(8) Å) is slightly shorter than those in other rhodium(I) complexes with P ligands having an olefin ligand in *trans* and a carbanion in *cis* position (median: 2.298 Å, lower/higher quartile: 2.278/2.325 Å, n = 15[60]). The bidentate binding of the co-ligands L_2 (dppe, **9c**·THF; cod, **11**, **12**)

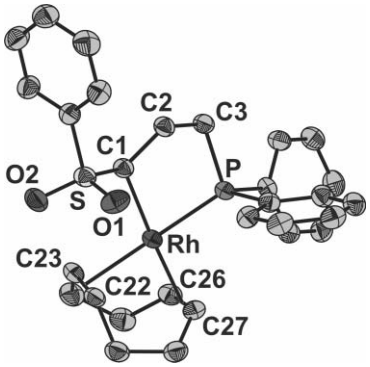


Fig. 5 Molecular structure of [Rh{CH(SO$_2$Ph)CH$_2$CH$_2$PPh$_2$-κ*C*,κ*P*}(cod)] in crystals of **11**. The ellipsoids are shown with a probability of 50%. H atoms have been omitted for clarity. Selected structural parameters (distances in Å, angles in °): Rh–P 2.264(8), Rh–C22/23$_{cg}$ (cg = center of gravity) 2.142(4), Rh–C1 2.181(3), Rh–C26/27$_{cg}$ 2.057(3), P–Rh–C26/27$_{cg}$ 95.3(2), C26/27$_{cg}$–Rh–C22/23$_{cg}$ 85.4(9), P–Rh–C1 81.3(7), C22/23$_{cg}$–Rh–C1 98.1(1), P–Rh–C22/23$_{cg}$ 177.8(2), C1–Rh–C26/27$_{cg}$ 175.4(7).

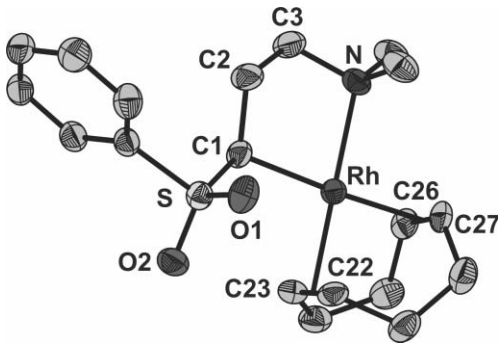


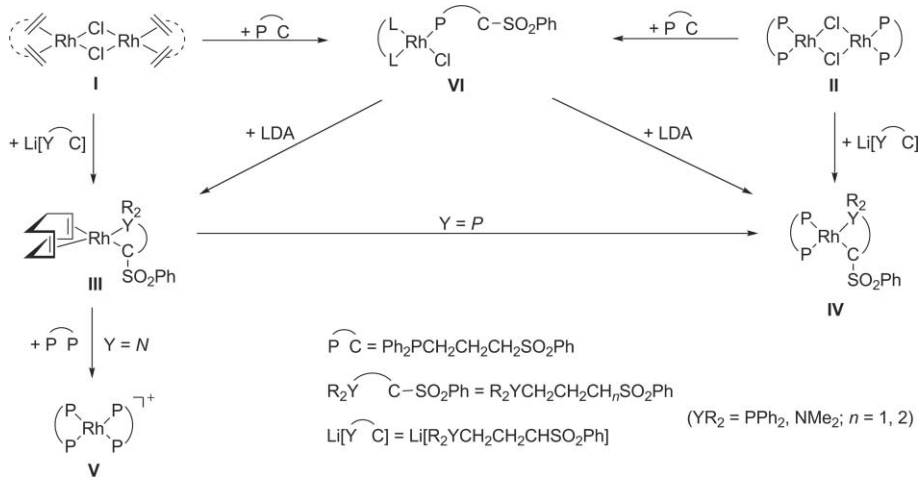
Fig. 6 Molecular structure of [Rh{CH(SO$_2$Ph)CH$_2$CH$_2$NMe$_2$-κ*C*,κ*N*}(cod)] in crystals of **12**. The ellipsoids are shown with a probability of 50%. H atoms have been omitted for clarity. Selected structural parameters (distances in Å, angles in °): Rh–N 2.175(3), Rh–C22/23$_{cg}$ 2.011(2), Rh–C1 2.149(3), Rh–C26/27$_{cg}$ 2.061(2), N–Rh–C26/27$_{cg}$ 94.6(7), C26/27$_{cg}$–Rh–C22/23$_{cg}$ 87.0(9), N–Rh–C1 81.6(1), C22/23$_{cg}$–Rh–C1 97.1(8), N–Rh–C22/23$_{cg}$ 176.5(7), C1–Rh–C26/27$_{cg}$ 174.0(8).

gives rise to slightly diminished P1–Rh–P2 (83.5(4)°, **9c**·THF) and C22/23$_{cg}$–Rh–C26/27$_{cg}$ (85.4(9)°, **11**; 87.0(9)°, **12**; cg = center of gravity) angles. The difference in the Rh–P bond lengths by 0.067 Å in **9c**·THF can be attributed to the difference in the *trans* influence of a neutral N and an anionic C ligand and is in the usual range.[61–63]

2.4 Conclusion

To summarize (Scheme 3), organorhodium inner complexes of the type [Rh{CH(SO$_2$Ph)CH$_2$CH$_2$YR$_2$-κ*C*,κ*Y*}L$_2$] (**III**, **IV**; YR$_2$ = PPh$_2$, NMe$_2$; L$_2$ = P⁀P, cod) were prepared by reactions of lithiated γ-phosphino- and γ-aminofunctionalized propyl phenyl sulfones with the requisite dinuclear complexes [(RhL$_2$)$_2$(μ-Cl)$_2$] (**I** → **III**, **II** → **IV**; Scheme 3). While in the case of the rhodaphosphacyclic complexes cod could be substituted by diphosphines (**III** → **IV**), the respective reactions of the azarhodacyclic complexes resulted with cleavage of both the organo ligands and the cod co-ligand only in the formation of cationic bis(diphosphine) complexes (**III** → **V**). Furthermore, chloridorhodium complexes with neutral PhSO$_2$CH$_2$CH$_2$CH$_2$PPh$_2$-κ*P* ligands were obtained in reactions of [(RhL$_2$)$_2$(μ-Cl)$_2$] (L$_2$ = P⁀P, cod, (C$_2$H$_4$)$_2$) with the phosphinofunctionalized sulfones (**I**/**II** → **VI**) whereas the aminofunctionalized sulfones did not react at all. Syntheses of type **VI** complexes opened up a way to prepare the inner complexes **III**/**IV** by deprotonation the *P* coordinated sulfone with LDA (**VI** → **III**/**IV**).

As shown here (**I**/**II** → **VI**) and as well known from numerous reactions described in literature[64] the cleavage of Rh–Cl–Rh bridges by phosphines proceeds smoothly under formation of phosphine rhodium complexes irrespective of the type of the phosphine. Although analogous reactions of [{Rh(cod)}$_2$(μ-Cl)$_2$] with pyridines, secondary amines and diamines have been described to proceed in most cases either with the formation of type [RhCl(cod)L] or [Rh(cod)L$_2$]$^+$ complexes, the tertiary aliphatic amine NEt$_3$ was found not to react at all.[65] Moreover, in analogous reactions of iminophosphoranes with dinuclear rhodium complexes [(RhL$_2$)$_2$(μ-Cl)$_2$] (L$_2$ = cod, (CO)$_2$) it was shown that the reactivity of these ligands strongly depends on the nucleophilicity of the *N* atom.[66,67] Furthermore, the ease



Scheme 3 Different routes to organorhodium inner complexes.

of cleaving Rh–N bonds as found in the reactions **III** → **V** (Scheme 3) was demonstrated on similar complexes by reaction of [RhCl(olefin)(*i*-PrPCH$_2$CH$_2$NMe$_2$-κ*P*,κ*N*)] with CO, C_2H_4 and H_2.[46] On the basis of all these findings the different reactivity of γ-phosphinopropyl and γ-aminopropyl phenyl sulfones towards dinuclear chloridobridged rhodium complexes can be understood. Thus, an easy access to a series of new organorhodium inner complexes bearing α-deprotonated sulfone ligands having an additional *P* or *N* donor site was found.

3. Experimental

3.1. General comments

All reactions and manipulations were carried out under argon using standard Schlenk techniques. Diethyl ether, toluene, *n*-pentane, and THF were dried over Na/benzophenone and freshly distilled prior to use. NMR spectra (^{1}H, ^{7}Li, ^{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; CD_3NO_2, δ_H 4.33, δ_C 62.8) as internal references; δ(^{7}Li) is relative to external LiCl (1 M in H_2O); 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 ("m") were obtained by using the PERCH NMR software package.[40] For couplings in ring systems only the shortest coupling path is given. Microanalyses (C, H, N) were performed in the Microanalytical Laboratory of the University of Halle using a CHNS-932 (LECO) as well as a VARIO EL elemental analyzer. [{Rh(cod)}$_2$(μ-Cl)$_2$] (**5**), [{Rh(C_2H_4)$_2$}$_2$(μ-Cl)$_2$] (**6**) and [{Rh(P⌒P)}$_2$(μ-Cl)$_2$] (**7a–d**) were prepared according to literature procedures.[68,45,69] Details of the preparation of starting compounds and a complete set of their NMR spectroscopic data are given in the ESI.† Li[CH(SO$_2$Ph)CH$_2$CH$_2$PPh$_2$] (**2**) and Li[CH(SO$_2$Ph)CH$_2$CH$_2$NMe$_2$] (**4**) were obtained by addition of *n*-BuLi (0.31 ml, 0.50 mmol, 1.6 M in *n*-hexane) at −78 °C to a solution of PhSO$_2$CHCH$_2$CH$_2$YR$_2$ (YR$_2$ = PPh$_2$, **1**; NMe$_2$, **3**; 0.50 mmol) in toluene (5 mL). Compounds **2** and **4** were used as obtained after stirring the reaction mixtures for 4 h at room temperature.

3.2. Preparation of [Rh{CH(SO$_2$Ph)CH$_2$CH$_2$PPh$_2$-κ*C*,κ*P*}(P⌒P)] (8a–d)

Route A. Li[CH(SO$_2$Ph)CH$_2$CH$_2$PPh$_2$] (**2**) (0.50 mmol) dissolved in toluene (5 mL) was added slowly *via* a syringe to a suspension of the respective rhodium complex [{Rh (μ-Cl)(P⌒P)}$_2$] (**7a–d**) (0.25 mmol) in toluene (5 mL) at −78 °C. After warming to room temperature the mixture was stirred overnight and filtered to separate the precipitated LiCl. The filtrate was reduced to half of its volume and *n*-pentane was added (5 mL). The resulted precipitate was filtered, washed with *n*-pentane (3 × 5 mL) and dried *in vacuo*.

Route B:. At −78 °C to a stirred suspension of the respective rhodium complex [{Rh(P⌒P)}$_2$(μ-Cl)$_2$] (**7a–d**) (0.25 mmol) in toluene (5 mL) PhSO$_2$CH$_2$CH$_2$CH$_2$PPh$_2$ (**1**) (184.2 mg, 0.50 mmol) in toluene (5 mL) was added *via* a syringe. Then the reaction mixture was stirred for 1 h at room temperature, cooled to −78 °C again and LDA (0.55 ml, 0.50 mmol, 0.91 M in THF) was slowly added. After warming to room temperature the mixture was stirred for 30 min. The precipitated LiCl was filtered, the filtrate was reduced to half of its volume and *n*-pentane (5 mL) was added. The precipitated compound was filtered, washed with *n*-pentane (3 × 5 mL) and dried *in vacuo*.

Route C. At room temperature to a stirred suspension of [{RhL$_2$}$_2$(μ-Cl)$_2$] (L$_2$ = cod, **5**; (C_2H_4)$_2$, **6**; 0.25 mmol) in toluene (5 mL) PhSO$_2$CH$_2$CH$_2$CH$_2$PPh$_2$ (**1**) (168.2 mg, 0.50 mmol) dissolved in toluene (10 mL) was added slowly. After stirring for 3 h the respective diphosphine P⌒P (0.50 mmol) dissolved in toluene (5 mL) was added. The reaction mixture was stirred for 3 h, at −78 °C LDA (0.55 mL, 0.50 mmol, 0.91 M in THF) was slowly added and stirred for further 30 min at room temperature. The precipitated LiCl was filtered, the filtrate was reduced to half of its volume and *n*-pentane (5 mL) was added. The precipitated compound was filtered, washed with *n*-pentane (3 × 5 mL) and dried *in vacuo*.

P⌒P = dmpe (**8a**). Yield: 229 mg (74%, route A). Found: C, 52.41; H, 5.73; Calcd. for $C_{46}H_{41}P_3SO_2Rh$ (620.48): C, 52.27; H, 5.85. ^{1}H NMR (400 MHz, THF-d_8): δ 0.79/0.91/1.65/1.69 (d/d/d/d, ^2J(^{1}H,^{31}P) = 7.5/7.5/8.3/8.3 Hz, 3H/3H/3H/3H, P(C*H*$_3$)$_2$), 1.18–1.44 (m, 2H, CHC*H*$_2$CH$_2$), 1.35–1.39/1.57–1.82 (m/m, 2H/2H, Me$_2$PC*H*$_2$C*H*$_2$PMe$_2$), 3.55 (s, br, 1H, C*H*SO$_2$Ph), 7.28–7.38 (m, 10H, *m*-, *p*-, *o*-H P*Ph*$_2$), 7.69–7.82 (m, 5H, *m*-, *p*-, *o*-*H* SO$_2$*Ph*). ^{13}C NMR (100 MHz, THF-d_8): δ 15.4/15.7/17.8/18.1 (d/d/d/d, ^1J(^{13}C,^{31}P) = 20.6/19.3/21.8/22.1 Hz, P*C*H$_3$), 30.3 (d, ^2J(^{13}C,^{31}P) = 19.5 Hz, CH*C*H$_2$CH$_2$), 31.5/31.7 ("d"/"d", *N* = 23.1/22.2 Hz Me$_2$P*C*H$_2$*C*H$_2$PMe$_2$), 36.5 (dd, ^1J(^{13}C,^{31}P) = 22.9 Hz, ^3J(^{13}C,^{31}P$_{trans}$) = 7.1 Hz, CHCH$_2$*C*H$_2$), 61.0–61.8 (m, *C*HSO$_2$Ph), 128.3–146.9 (C_{Ar}). ^{31}P NMR (81 MHz, THF-d_8): δ 35.5 (m, ^2J(^{31}P,^{31}P) = 34.9 Hz, ^2J(^{31}P,^{31}P) = 332.9 Hz, ^1J(^{31}P,^{103}Rh) = 144.8 Hz, *P* (dmpe) *trans* to P), 35.8 (m, ^2J(^{31}P,^{31}P) = 34.9 Hz, ^2J(^{31}P,^{31}P) = 29.9 Hz, ^1J(^{31}P,^{103}Rh) = 128.8 Hz, *P* (dmpe) *trans* to *C*), 58.0 (ddd, ^2J(^{31}P,^{31}P) = 29.9 Hz, ^2J(^{31}P,^{31}P) = 332.9, ^1J(^{31}P,^{103}Rh) = 144.3 Hz, CHCH$_2$CH$_2$*P*Ph$_2$).

P⌒P = dppm (**8b**). Yield: 377 mg (88%, route A). Found: C, 64.74; H, 5.09; Calcd for $C_{46}H_{42}P_3SO_2Rh$ (854.73): C, 64.64; H, 4.95. ^{1}H NMR (400 MHz, THF-d_8): δ 1.27–1.36/1.51–1.69 (m/m, 1H/1H, CHC*H*$_2$CH$_2$), 2.11/2.76 (m/m, 1H/1H, CHCH$_2$C*H*$_2$), 3.68 (m, 1H, C*H*SO$_2$Ph), 3.91–3.99/4.29–4.37, (m/m, 1H/1H, Ph$_2$PC*H*$_2$PPh$_2$), 6.94–8.06 (m, 35H, H_{Ar}).

^{13}C NMR (100 MHz, THF-d_8): δ 28.5 (d, ^2J(^{13}C,^{31}P) = 17.3 Hz, CH*C*H$_2$CH$_2$), 34.2 (dd, ^1J(^{13}C,^{31}P) = 23.3 Hz, ^3J(^{13}C,^{31}P$_{trans}$) = 4.7 Hz, CHCH$_2$*C*H$_2$), 48.6 ("t", *N* = 35.2 Hz, Ph$_2$P*C*H$_2$PPh$_2$), 61.6–62.6 (m, *C*HSO$_2$Ph), 125.0–145.2 (m, C_{Ar}). ^{31}P NMR (81 MHz, THF-d_8): δ–21.0 (ddd, ^2J(^{31}P,^{31}P) = 67.7 Hz, ^2J(^{31}P,^{31}P) = 340.5 Hz, ^1J(^{31}P,^{103}Rh) = 133.7 Hz, *P*(dppm) *trans* to P), 13.7 (ddd, ^2J(^{31}P,^{31}P) = 67.7 Hz, ^2J(^{31}P,^{31}P) = 32.1 Hz, ^1J(^{31}P,^{103}Rh) = 113.5 Hz, *P*(dppm) *trans* to *C*), 57.9 (ddd, ^2J(^{31}P,^{31}P) = 32.1 Hz, ^2J(^{31}P,^{31}P) = 340.58, ^1J(^{31}P,^{103}Rh) = 154.8 Hz, CHCH$_2$CH$_2$*P*Ph$_2$).

P⌒P = dppe (**8c**). Yield: 375 mg (86%, route A). Found: C, 64.32; H, 5.20; Calcd. for $C_{47}H_{44}P_3SO_2Rh$ (868.76): C, 64.98; H, 5.10. ^{1}H NMR (400 MHz, THF-d_8): δ 1.13–1.25/1.70–1.84 (m/m, 1H/1H, CHC*H*$_2$CH$_2$), 1.95–2.20/2.36–2.51 (m/m, 2H/2H, Ph$_2$PC*H*$_2$C*H*$_2$PPh$_2$), 2.21–2.30/2.99–3.09

(m/m, 1H/1H, $CHCH_2CH_2PPh_2$), 3.53 (s, br, 1H, $CHSO_2Ph$), 6.89–7.88 (m, 35H, H_{Ar}). ^{13}C NMR (100 MHz, THF-d_8): δ 27.0/30.2 (m/m, $CHCH_2CH_2/Ph_2PCH_2CH_2PPh_2$), 29.5 (d, $^2J(^{13}C,^{31}P)$ = 24.0 Hz, $CHCH_2CH_2$), 35.0 (dd, $^1J(^{13}C,^{31}P)$ = 22.2 Hz, $^3J(^{13}C,^{31}P_{trans})$ = 7.0 Hz, $CHCH_2CH_2$), 61.1–63.0 (m, $CHSO_2Ph$), 127.2–145.6 (C_{Ar}). ^{31}P NMR (81 MHz, THF-d_8): δ 55.5 (m, $^2J(^{31}P,^{31}P)$ = 31.7 Hz, $^2J(^{31}P,^{31}P)$ = 321.8 Hz, $^1J(^{31}P,^{103}Rh)$ = 153.1 Hz, $CHCH_2CH_2PPh_2$), 59.3 (m, $^2J(^{31}P,^{31}P)$ = 28.7 Hz, $^2J(^{31}P,^{31}P)$ = 31.7 Hz, $^1J(^{31}P,^{103}Rh)$ = 133.0 Hz, *P* (dppe) *trans* to *C*), 61.1 (m, $^2J(^{31}P,^{31}P)$ = 28.7 Hz, $^2J(^{31}P,^{31}P)$ = 321.8 $^1J(^{31}P,^{103}Rh)$ = 155.5 Hz, *P* (dppe) *trans* to P).

P⌒P = dppp (**8d**). Yield: 401 mg (91%, route A). Found: C, 65.55; H, 5.01; Calcd. for $C_{48}H_{46}P_3SO_2Rh$ (882.78): C, 65.31; H, 5.25. ^1H NMR (400 MHz, THF-d_8): δ 0.74–0.88/1.62–1.76 (m/m 1H/1H, $CHCH_2CH_2$), 1.21–1.42/2.01–2.09 (m/m, 1H/1H, $Ph_2PCH_2CH_2CH_2PPh_2$), 2.01–2.09/2.93 (m/m 1H/1H, $CHCH_2CH_2$), 2.13–2.25/2.70 (m/m 2H/2H, $Ph_2PCH_2CH_2CH_2PPh_2$), 2.81 (s, br, 1H, $CHSO_2Ph$), 6.55–8.08 (m, H_{Ar}). ^{13}C NMR (125 MHz, THF-d_8): δ 21.5 (s, $Ph_2PCH_2CH_2CH_2PPh_2$), 29.5 (d, $^2J(^{13}C,^{31}P)$ = 14.4 Hz, $CHCH_2CH_2$), 30.0/30.9 ("d"/"d", *N* = 23.6/18.5 Hz, $Ph_2PCH_2CH_2CH_2PPh_2$), 37.5 (dd, $^1J(^{13}C,^{31}P)$ = 23.8 Hz, $^3J(^{13}C,^{31}P_{trans})$ = 5.2 Hz, $CHCH_2CH_2$), 66.1–67.0 (m, $CHSO_2Ph$), 126.4–147.1 (m, C_{Ar}). ^{31}P NMR (81 MHz, THF-d_8): δ 16.3 (m, $^2J(^{31}P,^{31}P)$ = 25.8 Hz , $^2J(^{31}P,^{31}P)$ = 52.1 Hz, $^1J(^{31}P,^{103}Rh)$ = 127.1 Hz, *P* (dppp) *trans* to *C*), 19.5 (m, $^2J(^{31}P,^{31}P)$ = 52.1 Hz, $^2J(^{31}P,^{31}P)$ = 310.8 Hz, $^1J(^{31}P,^{103}Rh)$ = 150.1 Hz, *P* (dppp) *trans* to P), 55.6 (m, $^2J(^{31}P,^{31}P)$ = 25.8 Hz, $^2J(^{31}P,^{31}P)$ = 310.8, $^1J(^{31}P,^{103}Rh)$ = 156.0 Hz, $CHCH_2CH_2PPh_2$).

3.3. Preparation of [Rh{CH(SO_2Ph)$CH_2CH_2NMe_2$-κ*C*,κ*N*}(P⌒P)] (9a–d)

Complexes **9a–d** were obtained as described in 3.2 (route A) but using Li[CH(SO_2Ph)$CH_2CH_2NMe_2$] (**4**) (0.50 mmol) instead of **2**.

P⌒P = dmpe (**9a**). Yield: 114 mg (48%). Found: C, 43.01; H, 6.51; N, 2.92; Calcd. for $C_{17}H_{32}NP_2SO_2Rh$ (479.38): C, 42.60; H, 6.73; N, 2.86. ^1H NMR (400 MHz, THF-d_8): δ 1.31/1.44/1.56/1.62 (d/d/d/d, $^2J(^1H,^{31}P)$ = 6.2/6.3/9.3/9.6 Hz, 3H/3H/3H/3H, $P(CH_3)_2$), 1.50–1.66 (m, 4H, $Me_2PCH_2CH_2PMe_2$), 1.77–1.98 (m, 2H, $CHCH_2CH_2$), 2.14 (m, 2H, CH_2NMe_2), 2.61/2.71 (s/s, 3H/3H, $N(CH_3)_2$), 2.84–2.91 (m, 1H, $CHSO_2Ph$), 7.31–7.40 (m, 3H, *m*-, *p*-*H*, SO_2Ph), 7.74–7.83 2H, *o*-*H*, SO_2Ph). ^{13}C NMR (100 MHz, THF-d_8): δ 16.9–17.6 (m, $((CH_3)_2PCH_2CH_2P(CH_3)_2)$, 29.7–30.2/32.3–31.8 (m/m, $Me_2PCH_2CH_2PMe_2$), 30.6 (s, $CHCH_2CH_2$), 51.8/52.5 (s/s, $N(CH_3)_2$), 57.0 (ddd, $^2J(^{13}C,^{31}P_{cis})$ = 9.1 Hz, $^2J(^{13}C,\ ^{31}P_{trans})$ = 69.2 Hz, $^1J(^{13}C,^{103}Rh)$ = 25.5 Hz, $CHSO_2Ph$), 66.3 (s, CH_2NMe_2), 128.1 (s, *m*-*C*, SO_2Ph), 128.5 (s, *o*-*C*, SO_2Ph), 130.4 (s, *p*-*C*, SO_2Ph), 146.9 (s, *i*-*C*, SO_2Ph). ^{31}P NMR (81 MHz, THF-d_8): δ 28.3 (dd, $^2J(^{31}P,^{31}P)$ = 29.6 Hz, $^1J(^{31}P,^{103}Rh)$ = 148.2 Hz, *P trans* to *C*), 47.1 (dd, $^2J(^{31}P,^{31}P)$ = 29.6 Hz, $^1J(^{31}P,^{103}Rh)$ = 175.9 Hz, *P trans* to N).

P⌒P = dppm (**9b**). Yield: 258 mg (72%). Found: C, 60.69; H, 5.11; N, 2.01; Calcd. for $C_{36}H_{38}NP_2SO_2Rh$ (713.62): C, 60.59; H, 5.37; N, 1.96. ^1H NMR (500 MHz, THF-d_8): δ 1.29–1.45 (m, 2H, $CHCH_2CH_2$), 2.12–2.17/2.90–3.01(m/m, 1H/1H, $CHCH_2CH_2$), 2.23/2.78 (s/s, 3H/3H, $N(CH_3)_2$), 3.07 (m, $CHSO_2Ph$), 3.55–3.63/4.00–4.08 (m/m, 1H/1H, $Ph_2PCH_2PPh_2$), 7.07–8.14 (m, 25H, H_{Ar}). ^{13}C NMR (100 MHz, THF-d_8): δ 30.4 (s, $CHCH_2CH_2$), 51.7–52.2 (m, $Ph_2PCH_2PPh_2/N(CH_3)_2$), 57.1 (ddd, $^2J(^{13}C,^{31}P_{cis})$ = 7.0 Hz, $^2J(^{13}C,^{31}P_{trans})$ = 68.8 Hz, $^1J(^{13}C,^{103}Rh)$ = 27.1 Hz $CHSO_2Ph$), 65.8 (s, CH_2NMe_2), 127.3–146.4 (m, C_{Ar}). ^{31}P NMR (81 MHz, THF-d_8): δ –17.2 (dd, $^2J(^{31}P,^{31}P)$ = 83.7 Hz, $^1J(^{31}P,^{103}Rh)$ = 125.0 Hz, *P trans* to *C*),–1.7 (dd, $^2J(^{31}P,^{31}P)$ = 83.7 Hz, $^1J(^{31}P,^{103}Rh)$ = 165.5 Hz, *P trans* to N).

P⌒P = dppe (**9c**). Yield: 277 mg (76%). Found: C, 61.47; H, 5.54; N, 1.79; Calcd. for $C_{37}H_{40}NP_2SO_2Rh$ (727.66): C, 61.08; H, 5.50; N, 1.92. ^1H NMR (500 MHz, THF-d_8): δ 1.11–1.20/1.25–1.34 (m/m, 1H/1H, $CHCH_2CH_2$), 1.45–1.52/1.83–1.89/2.13–2.22/2.23–2.30 (m/m/m/m, 1H/1H/1H/1H, $Ph_2PCH_2CH_2PPh_2$), 2.10/3.23 (m/m, 1H/1H, $CHCH_2CH_2$), 2.17/2.48 (s/s, 3H/3H, $N(CH_3)_2$), 2.66 (s, br, $CHSO_2Ph$), 7.07–8.18 (m, 25H, H_{Ar}). ^{13}C NMR (100 MHz, THF-d_8): δ 30.2–30.6/34.2–34.8 (m/m, $Ph_2PCH_2CH_2PPh_2$), 30.4 (s, $CHCH_2CH_2$), 51.8/52.6 (s/s, $N(CH_3)_2$), 60.9 (ddd, $^2J(^{13}C,^{31}P_{cis})$ = 7.9 Hz, $^2J(^{13}C,^{31}P_{trans})$ = 67.9 Hz, $^1J(^{13}C,^{103}Rh)$ = 25.5 Hz, $CHSO_2Ph$), 66.3 (s, CH_2NMe_2), 126.1–146.2 (m, C_{Ar}). ^{31}P NMR (81 MHz, THF-d_8): δ 58.2 (dd, $^2J(^{31}P,^{31}P)$ = 30.1 Hz, $^1J(^{31}P,^{103}Rh)$ = 150.5 Hz, *P trans* to *C*), 76.0 (dd, $^2J(^{31}P,^{31}P)$ = 30.1 Hz, $^1J(^{31}P,^{103}Rh)$ = 188.1 Hz, *P trans* to N).

P⌒P = dppp (**9d**). Yield: 270 mg (73%). Found: C, 61.00; H, 5.74; N, 1.91; Calcd. for $C_{38}H_{42}NP_2SO_2Rh$ (741.69): C, 61.55; H, 5.71; N, 1.89. ^1H NMR (500 MHz, benzene-d_6): δ 1.34–1.55 (m, 2H/2H, $Ph_2PCH_2CH_2CH_2PPh_2/CHCH_2CH_2$), 1.79–1.83/1.92–2.02/2.20–2.28 (m/m/m, 1H/2H/1H, $Ph_2PCH_2CH_2CH_2PPh_2$), 2.15 (s, br, 6H, $N(CH_3)_2$), 2.31–2.40/2.60 (m/m, 1H/1H, $CHCH_2CH_2$), 3.20 (s, br, $CHSO_2Ph$), 6.86–8.49 (m, 25H, H_{Ar}). ^{13}C NMR (100 MHz, benzene-d_6): δ 19.4 (s, $Ph_2PCH_2CH_2CH_2PPh_2$), 28.2/28.9 (dd/dd, $^1J(^{13}C,^{31}P)$ = 29.7 Hz, $^2J(^{13}C,^{103}Rh)$ = 10.4 Hz/$^1J(^{13}C,^{31}P)$ = 26.3 Hz, $^2J(^{13}C,^{103}Rh)$ = 10.9 Hz $Ph_2PCH_2CH_2CH_2PPh_2$), 29.8 (s, $CHCH_2CH_2$), 53.85/53.89 (s/s, $N(CH_3)_2$), 61.4 (ddd, $^2J(^{13}C,^{31}P_{cis})$ = 8.9 Hz, $^2J(^{13}C,^{31}P_{trans})$ = 67.0 Hz, $^1J(^{13}C,^{103}Rh)$ = 26.4 Hz $CHSO_2Ph$), 66.4 (s, CH_2NMe_2), 127.0–145.8 (m, C_{Ar}). ^{31}P NMR (81 MHz, benzene-d_6): δ 14.2 (dd, $^2J(^{31}P,^{31}P)$ = 54.4 Hz, $^1J(^{31}P,^{103}Rh)$ = 141.3 Hz, *P trans* to *C*), 37.8 (dd, $^2J(^{31}P,^{31}P)$ = 54.4 Hz, $^1J(^{31}P,^{103}Rh)$ = 187.8 Hz, *P trans* to N).

3.4. Preparation of [RhCl(P⌒P)($Ph_2PCH_2CH_2CH_2SO_2Ph$-κ*P*)] (10a–d)

At room temperature to a stirred suspension of the respective rhodium complex [{Rh(P⌒P)}$_2$(μ-Cl)$_2$] (**7a–d**; 0.25 mmol) in toluene (5 mL) $PhSO_2CH_2CH_2CH_2PPh_2$ (**1**) (184.0 mg, 0.50 mmol) dissolved in toluene (3 mL) was added *via* a syringe and the mixture was stirred for 1 h. 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*.

P⌒P = dmpe (**10a**). Yield: 212 mg (65%). Found: C 50.90, H, 5.76; Calcd. for $C_{27}H_{37}ClP_3SO_2Rh$ (656.95): C, 49.37; H, 5.68. ^1H NMR (400 MHz, THF-d_8): 0.83/1.47 (d/d, $^2J(^1H,^{31}P)$ = 8.7/9.6 Hz, 6H/6H, $P(CH_3)_2$), 1.28–1.62 (m/m, 2H/2H, $Me_2PCH_2CH_2PMe_2$), 2.10–2.20 (m, 2H, $CH_2CH_2CH_2$), 2.58 (m, 2H, CH_2PPh_2), 3.88 ("t", *N* = 15.4 Hz, 2H, CH_2SO_2Ph), 7.06–7.92 (m, 15H, H_{Ar}). ^{13}C NMR (100 MHz, THF-d_8): 14.5/17.1 (d/d, $^1J(^{13}C,^{31}P)$ = 24.0/24.5 Hz, $P(CH_3)_2$), 20.7 (d, $^2J(^{13}C,^{31}P)$ = 5.2 Hz, $CH_2CH_2CH_2$), 26.0–26.5/34.5–35.2 (m/m,

$Me_2PCH_2CH_2PMe_2$), 27.6 (d, $^1J(^{13}C,^{31}P) = 20.9$ Hz, CH_2PPh_2), 58.2 (d, $^3J(^{13}C,^{31}P) = 10.3$ Hz, CH_2SO_2Ph), 125.9–141.6 (m, C_{Ar}). ^{31}P NMR (81 MHz, THF-d_8): δ 23.8 (m, $^2J(^{31}P,^{31}P) = 6.5$ Hz, $^2J(^{31}P,^{31}P) = 355.1$ Hz, $^1J(^{31}P,^{103}Rh) = 118.0$ Hz, PPh_2), 43.4 (m, $^2J(^{31}P,^{31}P) = 39.1$ Hz, $^2J(^{31}P,^{31}P) = 6.5$ Hz, $^1J(^{31}P,^{103}Rh) = 154.1$ Hz, *P* (dmpe) *trans* to *Cl*), 45.8 (m, $^2J(^{31}P,^{31}P) = 39.1$ Hz, $^2J(^{31}P,^{31}P) = 355.1$ Hz, $^1J(^{31}P,^{103}Rh) = 141.4$ Hz, *P* (dmpe) *trans* to P).

P⁀P = dppm (**10b**). Yield: 336 mg (75%). Found: C, 61.55; H, 4.83; Calcd. for $C_{46}H_{42}ClO_2P_3SRh$ (890.19): C, 62.07; H, 4.76. ^1H NMR (400 MHz, THF-d_8): δ 2.10 (m, 2H, $CH_2CH_2CH_2$), 2.37 (m, 2H, $CH_2CH_2CH_2PPh_2$), 3.36 ("t", *N* = 15.0 Hz, 2H, CH_2SO_2Ph), 3.93 ("t", *N* = 19.4 Hz, 2H, $PPh_2CH_2PPh_2$), 6.99–8.03 (m, 35H, H_{Ar}). ^{13}C NMR (100 MHz, THF-d_8): δ 19.7 (d, $^2J(^{13}C,^{31}P) = 5.2$ Hz, $CH_2CH_2CH_2$), 26.3 (d, $^1J(^{13}C,^{31}P) = 22.3$ Hz, $CH_2CH_2CH_2PPh_2$), 49.4 ("t", *N* = 42.6 Hz, $PPh_2CH_2PPh_2$), 56.8 (d, $^3J(^{13}C,^{31}P) = 12.7$ Hz, CH_2SO_2Ph), 127.9 (s, *m*-*C*, SO_2Ph), 128.0 (s, *p*-*C*, SO_2Ph), 128.8 (s, *o*-*C*, SO_2Ph), 140.5 (s, *i*-*C*, SO_2Ph), 127.3–136.5 (C_{Ar}). ^{31}P NMR (81 MHz, THF-d_8): δ –41.5 (ddd, $^2J(^{31}P,^{31}P) = 98.4$ Hz, $^2J(^{31}P,^{31}P) = 386.0$ Hz, $^1J(^{31}P,^{103}Rh) = 118.5$ Hz, *P* (dppm) *trans* to P), –15.5 (ddd, $^2J(^{31}P,^{31}P) = 32.1$ Hz, $^2J(^{31}P,^{31}P) = 98.4$ Hz, $^1J(^{31}P,^{103}Rh) = 156.0$ Hz, *P* (dppm) *trans* to *Cl*), 23.3 (ddd, $^2J(^{31}P,^{31}P) = 32.1$ Hz, $^2J(^{31}P,^{31}P) = 386.0$ Hz, $^1J(^{31}P,^{103}Rh) = 134.2$ Hz, $CH_2CH_2CH_2PPh_2$).

P⁀P = dppe (**10c**). Yield: 396 mg (88%). Found: C, 61.66; H, 5.11; Calcd. for $C_{47}H_{44}ClO_2P_3SRh$ (904.21): C, 62.43; H, 4.90. ^1H NMR (400 MHz, CD_2Cl_2): δ 1.77–1.89 (m, 2H, $CH_2CH_2CH_2$), 1.97–2.13 (m/m, 2H/2H, $PPh_2CH_2CH_2PPh_2$), 2.16–2.22 (m, 2H, $CH_2CH_2CH_2PPh_2$), 3.16 ("t", *N* = 14.8 Hz, 2H, CH_2SO_2Ph), 6.88–8.01 (m, 35H, H_{Ar})

^{13}C NMR (100 MHz, CD_2Cl_2): δ 20.1 (d, $^2J(^{13}C,^{31}P) = 5.1$ Hz, $CH_2CH_2CH_2$), 26.3/35.4 (m/m, $Ph_2PCH_2CH_2PPh_2$), 26.9 (d, $^1J(^{13}C,^{31}P) = 22.5$ Hz, $CH_2CH_2CH_2PPh_2$), 57.6 (d, $^3J(^{13}C,^{31}P) = 13.6$ Hz, CH_2SO_2Ph), 128.2 (s, *m*-*C*, SO_2Ph), 129.5 (s, *p*-*C*, SO_2Ph), 133.7 (s, *o*-*C*, SO_2Ph), 139.9 (s, *i*-*C*, SO_2Ph), 127.9–136.1 (C_{Ar}). ^{31}P NMR (81 MHz, THF-d_8): δ 23.7 (ddd, $^2J(^{31}P,^{31}P) = 35.6$ Hz, $^2J(^{31}P,^{31}P) = 351.5$ Hz, $^1J(^{31}P,^{103}Rh) = 131.6$ Hz, $CH_2CH_2CH_2PPh_2$), 58.9 (ddd, $^2J(^{31}P,^{31}P) = 33.4$ Hz, $^2J(^{31}P,^{31}P) = 351.5$ Hz, $^1J(^{31}P,^{103}Rh) = 140.2$ Hz, *P* (dppe) *trans* to P), 73.9 (ddd, $^2J(^{31}P,^{31}P) = 33.4$ Hz, $^2J(^{31}P,^{31}P) = 35.6$ Hz, $^1J(^{31}P,^{103}Rh) = 184.7$ Hz, *P* (dppe) *trans* to *Cl*).

P⁀P = dppp (**10d**). Yield: 382 mg (83%). Found: C, 61.77; H, 5.15; Calcd. for $C_{48}H_{47}ClO_2P_3SRh$ (919.25): C, 62.72; H, 5.15. ^1H NMR (400 MHz, THF-d_8): δ 1.64–1.79 (m, 2H, $PhSO_2CH_2CH_2CH_2PPh_2$), 2.11 (s, br, 2H/2H, $PhSO_2CH_2CH_2CH_2PPh_2/Ph_2PCH_2CH_2CH_2PPh_2$), 2.24 (s, br, 2H/2H, $Ph_2PCH_2CH_2CH_2PPh_2$), 3.49 ("t", *N* = 14.2 Hz, 2H, CH_2SO_2Ph), 6.82–7.94 (m, 35H, H_{Ar}). ^{13}C NMR (125 MHz, THF-d_8): δ 20.4 (s, $Ph_2PCH_2CH_2CH_2PPh_2$), 21.3 (d, $^2J(^{13}C,^{31}P) = 7.1$ Hz, $PhSO_2CH_2CH_2CH_2PPh_2$), 27.6–27.97/32.7 (m/m, $Ph_2PCH_2CH_2CH_2PPh_2$), 27.98 (d, $^1J(^{13}C,^{31}P) = 24.0$ Hz, $PhSO_2CH_2CH_2CH_2PPh_2$), 58.2 (d, $^3J(^{13}C,^{31}P) = 13.0$ Hz, CH_2SO_2Ph), 127.8–141.7 (C_{Ar}). ^{31}P NMR (81 MHz, THF-d_8): δ 12.9 (ddd, $^2J(^{31}P,^{31}P) = 56.4$ Hz, $^2J(^{31}P,^{31}P) = 349.0$ Hz, $^1J(^{31}P,^{103}Rh) = 132.5$ Hz, *P* (dppp) *trans* to P), 25.6 (ddd, $^2J(^{31}P,^{31}P) = 35.7$ Hz, $^2J(^{31}P,^{31}P) = 349.0$ Hz, $^1J(^{31}P,^{103}Rh) = 132.9$ Hz, 1P, $PhSO_2CH_2CH_2CH_2PPh_2$), 34.0 (ddd, $^2J(^{31}P,^{31}P) = 56.4$ Hz, $^2J(^{31}P,^{31}P) = 35.7$ Hz, $^1J(^{31}P,^{103}Rh) = 174.9$ Hz, *P* (dppp) *trans* to *Cl*).

3.5. Preparation of [Rh{CH(SO$_2$Ph)CH$_2$CH$_2$PPh$_2$-κ*C*,κ*P*}(cod)]·LiCl (11·LiCl)

Complex **11**·LiCl was obtained as described in 3.2 (route A) but using [{Rh(cod)}$_2$(μ-Cl)$_2$] (**5**) (123.3 mg, 0.25 mmol) instead of **7a–d**. Yield: 245 mg (79%).

Found: C, 56.72; H, 5.42; Calcd. for $C_{29}H_{32}PLiClSO_2Rh$ (620.91): C, 56.10; H, 5.19. ^1H NMR (400 MHz, THF-d_8): δ 1.87–2.60 (m, 8H/2H/2H, 4 × CH_2 (cod)/$CHCH_2CH_2/CH_2PPh_2$), 3.08/4.00/5.93/6.24 (m/m/m/m, 1H/1H/1H/1H, 4 × *CH* (cod)), 3.51 (m, 1H, $CHSO_2Ph$), 7.35–7.77 (m, 15H, H_{Ar}). ^{13}C NMR (100 MHz, THF-d_8): δ 29.4/29.9/32.6/33.4 (s/s/s/s, 4 × CH_2 (cod)), 29.7 (d, $^2J(^{13}C,^{31}P) = 13.3$ Hz, $CHCH_2CH_2$), 33.0 (d, $^1J(^{13}C,^{31}P) = 26.9$ Hz, CH_2PPh_2), 63.0 (dd, $^2J(^{13}C,^{31}P) = 4.6$ Hz, $^1J(^{13}C,^{103}Rh) = 29.1$ Hz, $CHSO_2Ph$), 80.1/80.9/100.3/100.8 (d/d/"t"/dd, $^1J(^{13}C,^{103}Rh) = 9.2$ Hz/$^1J(^{13}C,^{103}Rh) = 8.3$ Hz/*N* = 16.6 Hz/$^1J(^{13}C,^{103}Rh) = 12.0$ Hz, $^2J(^{13}C,^{31}P) = 6.7$ Hz, 4 × *CH* (cod)), 128.1–135.5 (C_{Ar}). ^{31}P NMR (80 MHz, THF-d_8): δ 52.0 (d, $^1J(^{31}P,\ ^{103}Rh) = 172.0$ Hz, PPh_2). ^7Li NMR (194 MHz, THF-d_8): δ 0.23 (s, *Li*Cl).

3.6. Preparation of [Rh{CH(SO$_2$Ph)CH$_2$CH$_2$NMe$_2$-κ*C*,κ*N*}(cod)]·LiCl (12·LiCl)

Complex **12**·LiCl was obtained as described in 3.2 (route A) but using Li[CH(SO$_2$Ph)CH$_2$CH$_2$NMe$_2$] (**4**) (0.50 mmol) and [{Rh(cod)}$_2$(μ-Cl)$_2$] (**5**) (123.3 mg, 0.25 mmol) instead of **2** and **7a–d**, respectively. Yield: 159 mg (66%).

Found: C, 47.83; H, 6.00; N, 2.96. Calcd. for $C_{19}H_{28}NSO_2LiClRh$ (479.80): C, 47.56; H, 5.88; N, 2.92. ^1H NMR (400 MHz, THF-d_8): δ 1.01–1.09/1.39–1.50/1.98–2.63 (m/m/m, 1H/1H/6H/2H, 4×CH_2 (cod)/CH_2PPh_2), 1.55–1.65 (m, 2H, $CHCH_2CH_2$), 2.74 (d"t", $^2J(^1H,^{103}Rh) = 2.5$ Hz/*N* = 5.4 Hz, 1H, $CHSO_2Ph$), 3.81/3.90/4.64/5.21 (m/m/m/m, 1H/1H/1H/1H, 4 × *CH* (cod)), 7.35–7.77 (m, 15H, H_{Ar}). ^{13}C NMR (100 MHz, THF-d_8): δ 28.74/29.7/31.6/34.1 (s/s/s/s, 4 × CH_2 (cod)), 30.6 (s, $CHCH_2CH_2$), 45.5/49.8 (s/s, $N(CH_3)_2$), 54.9 (d, $^1J(^{13}C,^{103}Rh) = 30.4$ Hz, $CHSO_2Ph$), 66.5 (s, CH_2NMe_2), 76.5/76.6/85.3/86.4 (d/d/d/dd, $^1J(^{13}C,^{103}Rh) = 7.9$ Hz/$^1J(^{13}C,^{103}Rh) = 7.8$ Hz/$^1J(^{13}C,^{103}Rh) = 10.1$ Hz/$^1J(^{13}C,^{103}Rh) = 9.2$ Hz, 4 × *CH* (cod)), 128.1 (s, *m*-*C*, SO_2Ph), 128.7 (s, *o*-*C*, SO_2Ph), 131.0 (s, *p*-*C*, SO_2Ph), 146.0 (s, *i*-*C*, SO_2Ph). ^7Li NMR (194 MHz, THF-d_8): δ 0.23 (s, *Li*Cl).

3.7. Preaparation of [RhCl(cod)(Ph$_2$PCH$_2$CH$_2$CH$_2$SO$_2$Ph-κ*P*)] (13)

Complex **13** was obtained as described in 3.4 but using [{Rh(cod)}$_2$(μ-Cl)$_2$] (**5**) (246.5 mg, 0.50 mmol) instead of **7a–d**. Yield: 511 mg (83%).

Found: C, 56.41; H, 5.97; Calcd. for $C_{29}H_{33}PClSO_2Rh$ (614.98): C, 56.65; H, 5.41. ^1H NMR (400 MHz, $CDCl_3$): δ 1.86/2.01/2.23–2.44 (m/m/m, 2H/2H/6H, $CH_2CH_2CH_2$ + 4 × CH_2 (cod)), 2.57 (m, 2H, CH_2PPh_2), 2.96/5.40 (s/s, br/br, 2H/2H, 4 × *CH* (cod)), 3.33 (m, 2H, CH_2SO_2Ph), 7.33–7.89 (m, 15H, H_{Ar}). ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.0 (d, $^2J(^{13}C,^{31}P) = 2.7$ Hz, $CH_2CH_2CH_2$), 26.6 (d, $^1J(^{13}C,^{31}P) = 25.2$ Hz, CH_2PPh_2), 28.72/28.73/32.9/33.0 (s/s/s/s, 4 × CH_2 (cod)), 57.1 (d, $^3J(^{13}C,^{31}P) = 13.8$ Hz, CH_2SO_2Ph), 70.6/105.3 (d/dd, $^1J(^{13}C,^{103}Rh) = 13.8$ Hz/$^1J(^{13}C,^{103}Rh) = 12.2$ Hz,

Table 3 Crystallographic data, data collection parameters, and refinement parameters for **9c**·THF, **10c**, **11**, and **12**

	9c·THF	**10c**	**11**	**12**
Empirical formula	$C_{37}H_{40}NO_2P_2RhS{\cdot}C_4H_8O$	$C_{47}H_{45}ClO_2P_3RhS$	$C_{29}H_{32}O_2PRhS$	$C_{19}H_{28}NO_2RhS$
M_r	799.71	905.16	578.49	437.39
Crystal System	Orthorhombic	Monoclinic	Triclinic	Orthorhombic
Space group	*Fdd*2	$P2_1/c$	$P\bar{1}$	*Pbca*
a/Å	30.109(3)	21.349(5)	9.3705(9)	12.2943(9)
b/Å	41.095(4)	16.099(5)	12.1565(11)	17.1678(16)
c/Å	12.580(3)	12.008(5)	12.6514(13)	17.2075(14)
α/°			63.954(7)	
β/°		94.237(5)	78.562(8)	
γ/°			77.146(7)	
V/Å^3	15565(4)	4116(2)	1254.0(2)	3631.9(5)
Z	16	4	2	8
D_c/g cm^{-1}	1.365	1.461	1.532	1.600
μ(Mo-Kα)/mm^{-1}	0.613	0.686	0.853	1.067
F(000)	6656	1864	596	1808
θ range/°	1.5–30.0	2.71–25.19	2.61–29.17	2.36–27.50
Rfln. collected	33 320	65 301	17 184	32 256
Refln. observed [$I > 2\sigma(I)$]	7229	3462	6075	3330
Rfln. independent	7652 ($R_{int} = 0.0665$)	7399 ($R_{int} = 0.1424$)	6724 ($R_{int} = 0.0322$)	4144 ($R_{int} = 0.0593$)
Data/restraints/parameters	7652/1/444	7399/0/496	6724/0/436	4144/0/330
Goodness-of-fit on F^2	1.126	0.7	1.110	1.025
R_1	0.0390	0.0325	0.0443	0.0392
wR_2 [$I > 2\sigma(I)$]	0.0837	0.0353	0.1188	0.0939
R_1	0.0428	0.1089	0.0488	0.0524
wR_2 (all data)	0.0854	0.0403	0.1215	0.1000
Largest diff. peak and hole/e Å^{-3}	0.597 and –0.431	0.409 and –0.563	0.825 and –1.112	0.709 and –0.830

$^2J(^{13}C,^{31}P) = 7.0$ Hz, 4 × *C*H (cod)), 127.9–137.2 (C_{Ar}). ^{31}P NMR (80 MHz, $CDCl_3$): *δ* 27.8 (d, $^1J(^{31}P, ^{103}Rh) = 149.2$ Hz, *P*Ph_2).

3.8. Preparation of [RhCl(C$_2$H$_4$)$_2$(Ph$_2$PCH$_2$CH$_2$CH$_2$SO$_2$Ph-κ*P*)] (14)

Complex **14** was obtained as described in 3.4 but using [{Rh(C$_2$H$_4$)$_2$}$_2$(μ-Cl)$_2$] (**6**) (194.5 mg, 0.50 mmol) instead of **7a–d** and using thf instead of toluene as solvent. Yield: 405 mg (72%). Found: C, 53.08; H, 5.25; Calcd. for $C_{25}H_{29}PClSO_2Rh$ (562.90): C, 53.34; H, 5.19. ^1H NMR (400 MHz, THF-d_8): *δ* 2.05/2.90 (s/s, br/br 4H/4H, 4 × =C*H*$_2$), 2.57 (m, 2H, C*H*$_2$PPh$_2$), 2.27 (s, br, 2H, CH$_2$C*H*$_2$CH$_2$), 2.42 (s, br, 2H, C*H*$_2$PPh$_2$), 3.27 (s, br, 2H, C*H*$_2$SO$_2$Ph), 7.35–7.87 (m, 15H, H_{Ar}). ^{13}C NMR (100 MHz, THF-d_8): *δ* 20.9 (s, br, CH$_2$*C*H$_2$CH$_2$), 28.2 (d, $^1J(^{13}C,^{31}P) = 29.4$ Hz, *C*H$_2$PPh$_2$), 48.2 (s, br, 4 × =*C*H$_2$), 57.3 (d, $^3J(^{13}C,^{31}P) = 14.2$ Hz, *C*H$_2$SO$_2$Ph), 128.8–414.2 (C_{Ar}). ^{31}P NMR (80 MHz, THF-d_8): *δ* 48.7 (d, br, $^1J(^{31}P, ^{103}Rh) = 186.1$ Hz, *P*Ph_2).

3.9. X-Ray crystallography

Data for X-ray diffraction analyses of single crystals of **9c**·THF, **11** and **12** were collected on a Stoe-IPDS 2T diffractometer at 200(2) K and of **10c** at 130(2) K on a CCD Oxford Xcalibur S diffractometer 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 3. Absorption corrections were applied numerically with X-RED32[70] (T_{min}/T_{max} 0.90/0.93, **11**; 0.84/0.95, **12**) and multi-scanning with SCALE3 ABSPACK[71] (T_{min}/T_{max} 0.90/1.00, **10c**), respectively. The structures were solved with direct methods using SHELXS-97[72] and refined using full-matrix least-square routines against F^2 with SHELXL-97.[73] All non-hydrogen atoms were refined with anisotropic displacement parameters and hydrogen atoms with isotropic ones. The positions of H atoms in **11** and **12** were found in the difference Fourier map and refined freely. H atoms in **9c** and **10c** were placed in calculated positions according to the riding model.

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