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Synthesis of a New Type of Water-Soluble Phosphines by Addition of Hydrophilic Thiols to Vinylphosphines. Preparation of the Rhodium and Palladium Complexes

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Dedicated to Prof. Dr. habil. Rudolf Taube on the Occasion of his 65th Birthday

Abstract. Commercially available ω-thioalkane sodium sulfonates could easily be added to mono-, bi- and trivinylphosphines. The two-phase system became homogeneous by stirring. The products (**1–6**, **11**) were characterized as phosphinoethyl-sulfonatoalkyl-thioethers with an unexpected high water solubility and with defined P/S ratios from 1/2, 1/4 and 1/6. All thioetherphosphines were characterized by ^{1}H, ^{13}C and ^{31}P NMR spectroscopy, IR spectroscopy and elemental analysis. Addition occurs only at pH >7 and in the absence of strong electrophiles to avoid the formation of phosphonium compounds. L-Cysteine ethyl ester (**8**) and 2-aminoethanethiol (**9**) react exclusively at the thiol group. The first complexes with Pd(II), Rh(III) and Rh(I) show a participation of the thioether group in the coordination.

The transfer of complex-catalyzed reactions into water as medium has been developed to a new field of research interesting for laboratory and industry [1]. One of the most important achievements is the hydroformylation process by Rhône-Poulenc and Ruhrchemie [2], but also some other processes are successfully realized in water [3]. A requirement of catalysis in water is the dispersibility of the catalyst in a molecular or colloidal range. Most common is the application of water-soluble phosphines as ligands [4]. The rhodium(I) complex used in industrial hydroformylation contains a threefold in *meta*-position sulfonated triphenylphosphine (TPPTS) synthesized by direct sulfonation with SO_3/H_2SO_4 [5]. A disadvantage of this method is the relatively low selectivity and the complicated separation of stepwise sulfonated phosphines, by-products like phosphinoxides [6] and the big amount of waste sulfuric acid. The low selectivity in sulfonation brings special problems by optically active arylphosphines [7]. Therefore, a lot of research has been done to develop unambiguous methods for the insertion of hydrophilic groups into phosphines. Alternatives are given by the alkylsulfonation of alkalimetal phosphides with propane- or butanesultone [8], with fluorophenylsulfonic acid derivatives [9] and with sulfonated halogenoalkanes [10].

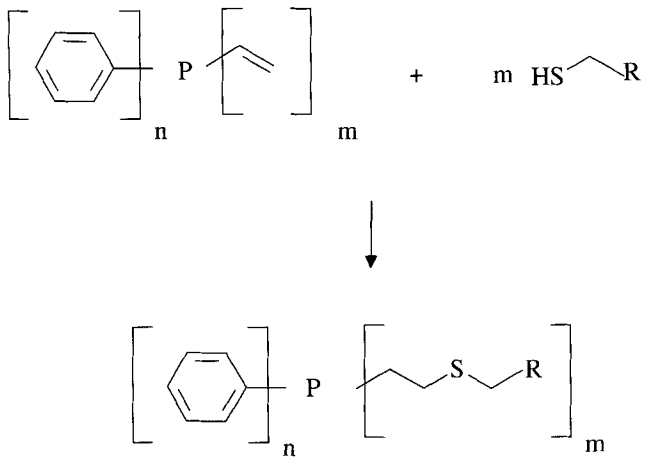
A possible way to *ortho*-sulfonatophenylphosphines is the reaction of chlorophosphines with *ortho*-lithiated lithium phenylsulfonates [11]. Some proposals exist for a more selective sulfonation of phenyl groups bound to phosphorus(III) by means of a spacer [12]. Nuzzo *et al.* [13] synthesized a series of water-soluble phosphines starting from bis-(β-diphenylphosphinoethyl)-amine by acylation with different anhydrides bearing hydrophilic groups. Alternatives for sulfonate groups are alkylated ammonium groups [14], polyether groups [15], carboxylate [16], and hydroxy groups [17]. The synthesis and application of water-soluble phosphines has been reviewed in a series of excellent articles [18].

We want to describe a new very convenient synthesis of highly water soluble phosphines containing thioether groups as further coordination sites by addition of sulfonated alkanethiols to vinylphosphines. Whereas the synthesis and the use of etherphosphines is well documented [19], only few ways exist for the synthesis of analogous thioetherphosphines. To our knowledge, the addition of thiols to vinylphosphines had been realized only by photochemical activation [20].

Results and Discussion

Sodium salts of ω-mercaptoalkane sulfonic acids react with vinylphosphines under mild conditions according to Scheme 1.

The polarity of the educts is rather different and requires a biphasic system for the conversion containing the vinylphosphine in the alcohol phase and the mercaptoalkanesulfonate in the water phase. The interface disappears within about 18 hours of powerful stirring



Compound	R	n	m
1	$-CH_2CH_2SO_3Na$	2	1
2	$-CH_2CH_2SO_3Na$	1	2
3	$-CH_2CH_2SO_3Na$	0	3
4	$-CH_2SO_3Na$	2	1
5	$-CH_2SO_3Na$	1	2
6	$-CH_2SO_3Na$	0	3
7	$-CH_2CH_2Si(OCH_3)_3$	2	1
8	$-CH(NH_2)COOC_2H_5$	2	1
9	$-CH_2NH_2$	2	1

In the same way compounds **10** and **11** were prepared by addition of one or two molecules of $HS(CH_2)_3SO_3Na$ to ethynyldiphenylphosphine.

10 $Ph_2P\text{-}CH{=}CHS(CH_2)_3SO_3Na$
11 $Ph_2P\text{-}CH_2\text{-}CH(S(CH_2)_3SO_3Na)_2$.

indicating the course of the reaction. Table 1 summarizes some properties of selected thioetherphosphines synthesized by this method.

The sodiumsulfonatoalkylphosphines **1–6** and **11** are characterized by solubility data. We observed an unexpectedly high solubility in the case of the threefold sulfonated phosphines **3** and **6**, which show a practically unlimited miscibility. The relative solubility indicates that the hydrophobic influence of a phenyl group is relatively higher than the hydrophilic influence of the sulfonate group. The finding is confirmed by compound **11** with two phenyl and two sulfonato groups, derived from diphenylethynylphosphine by addition of two molecules of sodium ω-mercaptopropane sulfonate. The addition of two molecules of ethanethiol to dibutylethynylphosphine was described by Voskuil *et al.* [21]. To our knowledge, the diphenylethynylphosphine adds the mercaptopropane sulfonate more slowly than the intermediate alkenylphosphine **10.** The mono-adduct **10** has been indicated only in a low concentration by ^{31}P NMR spectroscopy, whereas the bis-adduct **11** was isolated in a high yield.

The method presented here opens the way to water-soluble phosphines with unambiguous P/S ratios. The lowest ratio is 1:2 (compounds **1** and **4**) and the highest 1:6 (compounds **3** and **6**). The low-valent sulfur in the thioether group, should have the function of a coordinating group and the sulfur in the sulfonate group is responsible for the solubility in water.

A necessary condition for a successful addition of SH groups to unsaturated phosphines is the absence of protonated groups or other electrophiles. Attempting the addition of free mercaptoalkane sulfonic acids we obtained products with a signal of about $\delta = +16$ in the ^{31}P NMR spectrum indicating the presence of a phosphonium salt.The following neutralization with an equivalent amount of sodium hydroxide gave only partly the free phosphine. We suppose as a side reaction the addition of the protonated tertiary phosphine to the olefinic group [22]. Even the addition of cysteine as free carboxylic acid yields the phosphonium salt, whereas ethyl cysteinate reacts to **8** which exists as the thiol adduct indicated by a signal of $\delta = 28.6$ (d, $J_{C,P} = 21.2$ Hz) for C2 in the ^{13}C NMR spectrum (notation see experimental part) according to all investigated compounds. The addition of 2-aminoethanethiol to diphenylvinylphosphine shows the higher reactivity of thiol in comparison to amine. After 120 hours refluxing in ethanol as solvent we found 60 percent of the thioether **9,** but no indication to an amine adduct. Subsequent conversion of **9** with one equivalent of hydrochloric acid leads to a ^{31}P NMR signal at $\delta = +37$ indicating surprisingly a protonation of phosphorus.

The addition of thiols to vinylphosphines seems to be facilitated in presence of sulfonate groups, but it proceeds with a lower rate even with (3-mercaptopropyl)-

Table 1 Yields, solubilities in water and relative solubilities of phosphinoethylthioalkane sodiumsulfonates [a])

Compound	**1**	**2**	**3**	**4**	**5**	**6**	**11**
Yield (%)	97	90	63	95	83	59	60
Solubility g/l [a])	250	440	1860	325	540	2500	360
Relative Solubility	1	1.76	7.44	1.30	2.16	10.0	1.44

[a]) The solubilities were determined by evaporating of the water from the saturated solution.

tris-(methoxy)-silane (see product **7**) [23] and with β-D-thioglucosetetraacetate [24]. The silane **7** has been used as a convenient reagent to bind phosphine groups at silica gel and to immobilize transition metal complexes [23].

All alkylthioethyl-diphenylphosphines show ^{31}P signals near $\delta = -16$. Additional thioetheralkyl, thioetheralkenyl and bis-(thioetheralkyl) groups gave high field shifts.

The ^{1}H, ^{13}C and ^{31}P NMR data are given in the experimental part. The assignment of ^{1}H and ^{13}C signals were confirmed by recording the $^{1}H,^{1}H$ COSY and ^{13}C, ^{1}H correlation spectra.

The possible alternative NH-addition products in the case of compounds **8** and **9** could be excluded on the basis of ^{13}C chemical shifts. Only one NCH_2 signal (δ_{C4} = 40.5) was found for compound **9** and no NCH_2 for **8**, thus confirming that both compounds have the same thioether structure as in the other cases. The sensitivity of sulfonated phosphines against oxygen increases, as expected, with the number of alkyl groups (e.g. **1**<**2**<**3**). The above solid phosphines and all their solutions were handled under argon.

Complexes with palladium(II) and rhodium(III) or rhodium(I) were prepared in the following manner:

$$PdCl_2 + 2\ (\mathbf{1}) \longrightarrow Pd(\mathbf{1})_2Cl_2$$

$$K_2PdCl_4 + \mathbf{1} \longrightarrow Pd(\mathbf{1})Cl_2 \cdot 2\ KCl$$

$$RhCl_3 \cdot aq. + 2(\mathbf{1}) \longrightarrow Rh(\mathbf{1})(Ph_2PCH_2CH_2\text{-}SCH_2CH_2CH_2SO_3^-)Cl_2 \cdot aq.$$

$$Rh(COD)(acac) \xrightarrow[2.\ \mathbf{1}]{1.\ HBF_4} [(Rh(COD)(\mathbf{1})]BF_4$$

$$[(Rh(COD)_2]BF_4 + 2\ (\mathbf{4}) \longrightarrow [(Rh(\mathbf{4})_2]BF_4$$

Starting from $PdCl_2$ and K_2PdCl_4 with different amounts of phosphine **1**, complexes with a Pd : phosphine ratio of 1:2 and 1:1 could be prepared. In the first case only phosphorus, in the second example P and S should be involved in the coordination. ^{31}P NMR signals were found to be at $\delta = 63.8$ and $\delta = 73.2$. A rhodium(III) complex was formed from rhodium trichloride and two equivalents of phosphine **1** in water. The complex contained only two chlorides and one sodium as cation indicating that one chloride is substituted by sulfonate. The P-Rh coupling in ^{31}P NMR with $J_{Rh,P}$ = 108.3 Hz shows single coordination to P in accordance to Sanger [25].

Two types of rhodium(I) complexes were synthesized: the mono-(phosphine) complex by stepwise reaction of 1.5-cyclooctadiene-rhodium(I) acetylacetonate with HBF_4 and one equivalent of phosphine **1**, and the bis-(phosphine) complex by reaction of bis-(1.5-cyclooctadiene)-rhodium(I) tetrafluoroborate with two equivalents of phosphine **4**. The ^{31}P NMR spectra show $J_{Rh,P}$ = 147.7 Hz for the mono- and $J_{Rh,P}$ = 160.0 Hz for the bis-(phosphine) complex indicating chelates with P∩S coordination. The BF_4^- group was detected by ^{19}F NMR ($\delta = -148.6$ and -152.7, respectively).

Ligands with P and S as coordination sites have a general interest in homogeneous catalysis [26] especially with optically active groups for asymmetric induction [27], but only moderate enantiomeric excesses could be observed [28].

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Experimental

Chemicals. The following chemicals were purchased: 2-Aminoethanethiol, vinylmagnesium bromide THF-solution (Aldrich), vinylmagnesium chloride THF-solution (Acros), chlorodiphenylphosphine (Avocado), 2-mercaptoethane sulfonic acid sodium salt and 3-mercaptopropane sulfonic acid sodium salt, 3-mercaptopropyl-trimethoxy-silane, L-cysteine, L-cysteine hydrochloride, L-cysteine ethyl ester hydrochloride (Fluka).

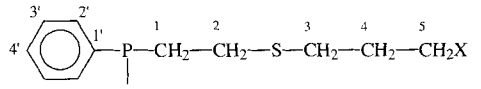
All syntheses were performed in oxygen-free solvents under argon atmosphere. The reactions were controlled by ^{31}P NMR spectroscopy.

Vinyldiphenylphosphine was synthesized as described in Ref. [29] from chloro-diphenylphosphine and vinylmagnesium bromide THF-solution. The temperature during addition of the phosphine needs to be lower than 25 °C and only the half quantity of ammonium chloride solution was used. Toluene was used instead of benzene. Yield: 76%.

Trivinyl- and divinylphenylphosphine were prepared according to Ref. [30]. Vinyl-magnesium chloride in THF was cooled at −10 °C and the corresponding chlorophosphines were added carefully to keep the temperature near 0 °C. Trivinylphosphine must be stored with hydroquinone.

Ethynyldiphenylphosphine was prepared as described in Ref. [31], and the sodium salts of ω-mercaptoalkanesulfonic acids to vinylphosphines was added as described previously [32].

The ^{1}H, ^{13}C, ^{19}F, ^{29}Si and ^{31}P NMR spectra were recorded on Bruker Spectrometers AC 250 and ARX 300. The ^{1}H, ^{13}C and ^{29}Si chemical shifts are referred to TMS, the ^{19}F chemical shifts to $CFCl_3$ and the ^{31}P chemical shifts to 85% H_3PO_4. All δ values are given in ppm. The calibration of the ^{1}H and ^{13}C NMR spectra was carried out by means of solvent peaks: DMSO-d_6: $\delta(^{1}H) = 2.50$; $\delta(^{13}C) = 39.7$; C_6D_6: $\delta(^{1}H) = 7.16$; $\delta(^{13}C) = 128.7$ or in D_2O solution by using dioxane as internal standard (δ (^{1}H) 3.71; δ (^{13}C) 67.6).



IR spectra of the phosphines were obtained on a Nicolet Magna 550 as KBr disks or dispersed in nujol mull. The mass spectrometry was performed on an AMD 402/3 by means of FAB. Yields are given in Tab. 1.

General procedure of synthesis of phosphinoethyl-sulfonatoalkyl-thioethers (1–6)

To a solution of 10 mmol of each vinylphosphine in 10 ml ethanol the corresponding amounts of sodium mercaptoalkane sulfonates (10, 20 or 30 mmol) in 10 ml water were added. Both phases were rapidly stirred at room temperature for < 18 hours. During this time the reaction was finished and the interphase disappeared. The solvents were evaporated, the residue washed several times with ether, reprecipitated from water/ethanol or water/methanol and dried *in vacuo* at 80 °C for some days.

2-(3-Sodiumsulfonatopropyl)thioethyl-diphenylphosphine (**1**)

$C_{17}H_{20}O_3NaPS_2$ (390.43): calcd. C 52.29 H 5.16 P 7.93 S 16.42; found C 51.98 H 5.23 P 7.99 S 16.30. – ^{1}H NMR (D_2O): δ 7.10 (m, 2'-C_6H_5); 6.90 (m, 3'-C_6H_5, 4'-C_6H_5); 2.70 (m, 5-CH_2); 2.25 (m, 2-CH_2, 3-CH_2); 2.00 (m, 1-CH_2); 1.73 (m, 4-CH_2). – ^{13}C NMR (D_2O): δ 138.4 (d, $^1J_{P,C}$ = 11.7 Hz, C-1'); 133.6 (d, $^2J_{P,C}$ = 18.6 Hz, C-2'); 129.8 (C-4'); 129.6 (d, $^3J_{P,C}$ = 6.7 Hz, C-3'); 51,0 (C-5); 31.3 (C-3); 29.1 (d, $^2J_{P,C}$ = 20.2 Hz, C-2); 29.0 (d, $^1J_{P,C}$ = 13.1 Hz, C-1); 25.2 (C-4). – ^{31}P NMR (D_2O): δ –17.3.

Bis-[2-(3-sodiumsulfonatopropyl)thioethyl]-phenylphosphine (**2**)

$C_{16}H_{25}O_6Na_2PS_4$ (518.55): calcd. C 37.06 H 4.86 P 5.97 S 24.73; found C 36.54 H 5.03 P 5.67 S 24.18. – ^{1}H NMR (D_2O): δ 7.55 (m, 2'-C_6H_5); 7.40 (m, 3'-C_6H_5, 4'-C_6H_5); 2.86 (m, 5-CH_2); 2.57 (m, 3-CH_2); 2.53 (m, 2-CH_2); 2.02 (m, 1-CH_2); 1.85 (m, 4-CH_2). – ^{13}C NMR (D_2O): δ 136.6 (d, $^1J_{P,C}$ = 9.7 Hz, C-1'); 133.8 (d, $^2J_{P,C}$ = 18.4 Hz, C-2'); 130.9 (C-4'); 130.0 (d, $^3J_{P,C}$ = 7.4 Hz, C-3'); 50.8 (C-5); 30.7 (C-3); 28.3 (d, $^2J_{P,C}$ = 16.1 Hz, C-2); 28.0 (d, $^1J_{P,C}$ = 9.5 Hz, C-1); 25.0 (C-4). – ^{31}P NMR (D_2O): δ –26.1.

Tris-[2-(3-sodiumsulfonatopropyl)thioethyl]-phosphine (**3**)

$C_{15}H_{30}O_9Na_3PS_6$ (646.69): calcd. C 27.85 H 4.67 P 4.76 S 29.74; found C 27.41 H 5.16 P 4.10 S 29.25. – ^{1}H NMR (D_2O): δ 2.78 (m, 5-CH_2); 2.70 (m, $^3J_{P,H-2}$ = 6.9 Hz, 2-CH_2, 3-CH_2); 1.98 (m, 4-CH_2); 1.83 (m, $^2J_{P,H-1}$ = 2.0 Hz, 1-CH_2). – ^{13}C NMR (D_2O): δ 50.9 (C-5); 31.0 (C-3); 28.7 (d, $^2J_{P,C}$ = 16.0 Hz, C-2); 26.7 (d, $^1J_{P,C}$ = 12.0 Hz, C-1); 25.2 (C-4). – ^{31}P NMR (D_2O): δ –29.1.

2-(2-Sodiumsulfonatoethyl)thioethyl-diphenylphosphine (**4**)

$C_{16}H_{18}O_3NaPS_2$ (376.40): calcd. C 51.05 H 4.82 P 8.23 S 17.04; found C 50.79 H 5.05 P 7.91 S 17.70. – ^{1}H NMR (D_2O): δ 7.10 (m, 2'-C_6H_5); 6.92 (m, 3'-C_6H_5, 4'-C_6H_5); 2.88 (m, 4-CH_2); 2.70 (m, 3-CH_2); 2.30 (m, $^3J_{P,H-2}$ = 6.5 Hz, 2-CH_2); 2.04 (m, $^2J_{P,H-1}$ = 1.3 Hz, 1-CH_2). – ^{13}C NMR (D_2O): δ 138.4 (d, $^1J_{P,C}$ = 11.9 Hz, C-1'); 133.6 (d, $^2J_{P,C}$ = 18.5 Hz, C-2'); 129.8 (C-4'); 129.6 (d, $^3J_{P,C}$ = 6.7 Hz, C-3'); 52.1 (C-4); 29.0 (d, $^2J_{P,C}$ = 20.1 Hz, C-2); 28.6 (d, $^1J_{P,C}$ = 12.9 Hz, C-1); 27.1 (C-3). – ^{31} P NMR (D_2O): δ –17.1.

Bis-[2-(2-sodiumsulfonatoethyl)thioethyl]-phenylphosphine (**5**)

$C_{14}H_{21}O_6Na_2PS_4$ (490.39): calcd. C 34.28 H 4.32 P 6.31 S 26.14; found C 33.95 H 4.52 P 6.45 S 26.57. – ^{1}H NMR (D_2O): δ 7.57 (m, 2'-C_6H_5); 7.42 (m, 3'-C_6H_5, 4'-C_6H_5); 3.00 (m, 4-CH_2); 2.80 (m, 3-CH_2); 2.55 (m, 2-CH_2); 2.05 (m, 1-CH_2). – ^{13}C NMR (D_2O): δ 136.5 (d, $^1J_{P,C}$ = 11.0 Hz, C-1'); 133.6 (d, $^2J_{P,C}$ = 18.8 Hz, C-2'); 130.7 (C-4'); 129.9 (d, $^3J_{P,C}$ = 7.5 Hz, C-3'); 51.9 (C-4); 28.7 (d, $^2J_{P,C}$ = 16.9 Hz, C-2); 27.8 (d, $^1J_{P,C}$ = 10.8 Hz, C-1); 26.5 (C-3). – ^{31}P NMR (D_2O): δ –25.7.

Tris-[2-(2-sodiumsulfonatoethyl)thioethyl]-phosphine (**6**)

$C_{12}H_{24}O_9Na_3PS_6$ (604,58): calcd. C 23.83 H 4.01 P 5.12 S 31.81; found C 23.58 H 4.43 P 4.85 S 32.40. – ^{1}H NMR (D_2O): δ 3.12 (m, 4-CH_2); 2.90 (m, 3-CH_2); 2.72 (m, 2-CH_2); 1.85 (m, 1-CH_2). – ^{13}C NMR (D_2O): δ 52.0 (C-4); 29.0 (d, $^2J_{P,C}$ = 15.9 Hz, C-2); 26.6 (C-3); 26.4 (d, $^1J_{P,C}$ = 11.5 Hz, C-1). – ^{31}P NMR (D_2O): δ –29.5.

2-(3-Trimethoxysilylpropyl)thioethyl diphenylphosphine (**7**)

To a solution of 1.96 g (10 mmol) of thiopropyltrimethoxysilane in 10 ml absolute THF 2.12 g (10 mmol) of vinyldiphenylphosphine were added and refluxed for 8 hours. The solvents were evaporated under vacuum at 150 °C. After cooling to room temperature the residue was extracted with ether and dried *in vacuo*. Yields 3.35 g (82 %). – $C_{20}H_{29}O_3PSSi$ (408.55): calcd. C 58.80 H 7.15 P 7.58 S 7.85; found C 58.96 H 6.88 P 7.90 S 8.32. – ^{1}H NMR (C_6D_6): δ 7.58 (m, 2'-C_6H_5); 7.28 (m, 3'-C_6H_5, 4'-C_6H_5); 3.59 (s, OCH_3); 2.73 (m, 2-CH_2); 2.56 (m, 3-CH_2); 2.46 (m, 1-CH_2); 1.86 (m, 4-CH_2); 0.89 (m, 5-CH_2). – ^{13}C NMR (C_6D_6): δ 139.6 (d, $^1J_{P,C}$ = 15.1 Hz, C-1'); 133.7 (d, $^2J_{P,C}$ = 18.6 Hz, C-2'); 129.5 (C-4'); 129.4 (d, $^3J_{P,C}$ = 6.5 Hz, C-3'); 51.0 (OCH_3); 35.8 (C-3); 30.0 (d, $^1J_{P,C}$ = 15.6 Hz, C-1); 29.3 (d, $^2J_{P,C}$ = 21.3 Hz, C-2); 24.0 (C-4); 9.6 (C-5). – ^{31}P NMR (C_6D_6): δ –16.2. – ^{29}Si NMR (C_6D_6): δ –42.7.

(2-Diphenylphosphinoethyl)-L-cysteine ethyl ester (**8**)

276 mg (12 mmol) of sodium were dissolved in 20 ml ethanol and 2.23 g (12 mmol) of L-cysteine ethylesterhydrochloride were added. The mixture was stirred for half an hour and, after that, the precipitate of NaCl was separated by capillary filtration. 2.54 g (12 mmol) of vinyldiphenylphosphine were added to the filtered solution. The reaction was continued for five days at 50 °C. After removing the solvent the residue was dissolved in 20 ml methanol. Addition of 50 ml water yielded a brown oil, which was separated and dried *in vacuo*. Yield 3.84 g (92%) $[\alpha]_D$ = + 8.8 (c = 2.0/EtOH). – $C_{19}H_{24}O_2NPS$ (361.42): calcd. C 63.14 H 6.70 N 3.87 P 8.57 S 8.87, found C 62.74 H 6.94 N 3.60 P 8.31 S 8.32. – ^{1}H NMR (DMSO-d_6): δ 7.40 (m, 10 H, C_6H_5); 4.00 (q, $^3J_{CH2,CH3}$ = 7.1 Hz, OCH_2); 3.44 (t, $^3J_{H-3,H-4}$ = 6.2 Hz, 4-CH); 2.71 (d, $^3J_{H-3,H-4}$ = 6.2 Hz, 3-CH_2); 2.50 (m, 2-CH_2); 2.30 (m, 1-CH_2); 1.83 (b, 2H, NH_2); 1.10 (t, $^3J_{CH2,CH3}$ = 7.1 Hz, CH_3). – ^{13}C NMR (DMSO-d_6): δ 174.0 (COO); 137.9 (d, $^1J_{P,C}$ = 14.3 Hz, C-1');

132.5 (d, $^2J_{P,C}$ = 18.6 Hz, C-2'); 128.9 (C-4'); 128.8 (d, $^3J_{P,C}$ = 6.6 Hz, C-3'); 60.2 (OCH_2); 54.6 (C-4); 36.6 (C-3); 28.6 (d, $^2J_{P,C}$ = 21.2 Hz, C-2); 27.9 (d, $^1J_{P,C}$ = 14.3 Hz, C-1); 14.1 (CH_3). – ^{31}P NMR (DMSO-d_6): δ –16.5.

2-(2-Aminoethyl)thioethyl-diphenylphosphine (**9**)

230 mg (10 mmol) of sodium were dissolved in 20 ml ethanol and 1.04 g (10 mmol) of 2-aminoethanethiol-hydrochloride were added. After stirring the mixture for half an hour the precipitate of NaCl was separated by capillary filtration. 2.12 g (10 mmol) of vinyldiphenylphosphine were added to the filtered solution and the reaction mixture was refluxed for five days. The ethanol was removed and the residue dissolved in toluene. After filtration and evaporation of toluene *in vacuo* a brownish oil was obtained. Yield 1.62 g (56%). – MS *m/e* = 290 (M+1). – $C_{16}H_{20}NPS$ (289.37): calcd. C 66.40 H 6.97 N 4.84 P 10.70 S 11.08, found C 66.12 H 6.73 N 4.41 P 10.57 S 10.89. – IR: no SH band. – ^{1}H NMR (DMSO-d_6): δ 7.35 (m, 10H, C_6H_5); 4.00 (b, 2H, NH_2); 2.68 (m, 4-CH_2); 2.57 (m, 3-CH_2); 2.47 (m, 2-CH_2); 2.32 (m, 1-CH_2). – ^{13}C NMR (DMSO-d_6): δ 137.9 (d, $^1J_{P,C}$ = 14.3 Hz, C-1'); 132.5 (d, $^2J_{P,C}$ = 18.8 Hz, C-2'); 128.9 (C-4'); 128.7 (d, $^3J_{P,C}$ = 6.6 Hz, C-3'); 40.5 (C-4); 32.9 (C-3); 27.8 (d, $^1J_{P,C}$ = 14.1 Hz, C-1); 27.6 (d, $^2J_{P,C}$ = 21.0 Hz, C-2). – ^{31}P NMR (DMSO-d_6): δ –16.0.

2.2-Bis-(3-sodiumsulfonatopropyl)thioethyl-diphenylphosphine (**11**)

To a solution of 2.10 g (10 mmol) of ethynyldiphenylphosphine in 10 ml ethanol 3.56 g (20 mmol) of 3-mercaptopropanesulfonate in 10 ml water were added. Both phases were refluxed for 48 hours. The ^{31}P NMR spectrum showed only a small signal at δ = –25 for the *mono*-addition product $Ph_2PCH{=}CH\text{-}S\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}SO_3Na$ (**10**), which disappeared gradually. The precipitate forming at the same time was separated by capillary filtration, washed with ether and dried *in vacuo*. – $C_{20}H_{25}O_6Na_2PS_4$ (566.59): calcd. C 42.39 H 4.45 P 5.47 S 22.63; found C 42.20 H 4.53 P 5.11 S 22.23. – ^{1}H NMR (D_2O): δ 7.33 (m, 2'-C_6H_5); 7.22 (m, 3'-C_6H_5, 4'-C_6H_5); 3.71 (dt, $^3J_{P,H\text{-}2}$ = 8.0 Hz, $^3J_{H\text{-}1,H\text{-}2}$ = 7.2 Hz, 2-CH); 2.84 (m, 5-CH_2); 2.56 (m, 1-CH_2, 3-CH_2); 1.86 (m, 4-CH_2). – ^{13}C NMR (D_2O): δ 138.2 (d, $^1J_{P,C}$ = 11.1 Hz, C-1'); 133.8 (d, $^2J_{P,C}$ = 19.0 Hz, C-2'); 130.3 (C-4'); 129.9 (d, $^3J_{P,C}$ = 6.9 Hz, C-3'); 51.0 (C-5); 49.6 (d, $^2J_{P,C}$ = 18.2 Hz, C-2); 36.9 (d, $^1J_{P,C}$ = 13.1 Hz (C-1); 30.4 (C-3); 25.1 (C-4). – ^{31}P NMR (D_2O): δ –20.6.

Rhodium and Palladium Complexes

Bis-[2-(3-sodiumsulfonatopropyl)thioethyl-diphenylphosphine]-dichloro-palladium(II)

177 mg (1 mmol) of $PdCl_2$ and 781 mg (2 mmol) of **1** were dissolved in 8 ml water at 80 °C. A grey–greenish precipitation was obtained. After stirring the mixture for three hours, the solvent was removed by capillary filtration and the residue recrystallized from 20 ml methanol and dried *in vacuo*. Yield 441 mg (46 %). – $C_{34}H_{40}O_6Cl_2Na_2P_2PdS_4$ (958.01): calcd. C 42.62 H 4.21 Cl 7.40 P 6.47 Pd 11.11 S 13.39; found C 42.17 H 4.19 Cl 7.92 P 6.02 Pd 10.8 S 13.70. – ^{31}P NMR (D_2O): δ 63.8.

[2-(3-Sodiumsulfonatopropyl)thioethyl-diphenylphosphine]-dichloro-palladium(II)

390 mg (1 mmol) of **1** and 326 mg (1 mmol) of K_2PdCl_4 were dissolved each in 2 ml water and stirred for two hours at room temperature. The dark solution was concentrated and the yellow powder precipitated with methanol was separated and dried *in vacuo*. Yield 652 mg (91%). – $C_{17}H_{20}O_3Cl_2NaPPdS_2 \cdot 2KCl$ (716.61): calcd. C 28.49 H 2.81 Cl 19.79 P 4.32 Pd 14.08 S 8.94; found C 28.10 H 2.88 Cl 19.90 P 4.05 Pd 14.0 S 8.85. – ^{31}P NMR (D_2O): δ 73.2.

Bis-[2-(3-sodiumsulfonatopropyl)thioethyl-diphenylphosphine]-dichloro-rhodium(III)

264 mg (1 mmol) of $RhCl_3 \cdot 3H_2O$ and 781 mg (2 mmol) of **1** were dissolved in 5 ml water. The red solution was stirred for one hour until a precipitate was observed. The precipitate was separated and recrystallized with methanol. Yield 590 mg (61%). – $C_{34}H_{40}O_6Cl_2NaP_2RhS_4 \cdot 2H_2O$ (967.68): calcd. C 42.20 H 4.58 Cl 7.32 P 6.40 Rh 10.63 S 13.25; found C 41.09 H 4.32 Cl 7.48 P 6.72 Rh 10.00 S 13.47. – ^{31}P NMR (D_2O): δ 40.1(d, $J_{Rh,P}$ = 108.3 Hz).

[2-(3-Sodiumsulfonatopropyl)thioethyl-diphenylphosphine]-(1.5-cyclooctadiene)-rhodium(I) tetrafluoroborate

155 mg (0.50 mmol) (1,5-cyclooctadiene)-rhodium acetylacetonate were dissolved in 2 ml THF, after which 100 µl HBF_4-etherate were added, and the mixture was stirred for 30 min at room temperature. 214.5 mg (0.55 mmol) of **1** were dissolved in 6 ml abs. methanol. Both solutions were mixed and stirred overnight. After capillary filtration the solvents were removed and the residue was dried *in vacuo* at 100 °C. Yield 278 mg (81%). – $C_{25}H_{32}O_3PBF_4NaRhS_2$ (688.31): calcd. C 43.62 H 4.69 P 4.50 Rh 14.95 S 9.32; found C 43.14 H 4.87 P 4.33 Rh 14.76 S 9.05. – ^{31}P NMR (DMSO-d_6): δ 58.7 (d, $J_{Rh,P}$ = 147.7 Hz). – ^{19}F NMR (DMSO-d_6): δ = –148.6.

Bis-[2-(3-sodiumsulfonatoethyl)thioethyl-diphenylphosphine]-rhodium(I) tetrafluoroborate

406 mg (1 mmol) of $[Rh(COD)_2]BF_4$ were dissolved in 4 ml methanol and added to 697 mg (2 mmol) of **4** in 5 ml water. The mixture was stirred for 3 hours at room temperature. The phase separation disappears within 10 min. After capillary filtration the solvents were removed and the residue was dried *in vacuo* at 100 °C. Yield 744 mg (78%). – $C_{32}H_{36}O_6BF_4Na_2P_2RhS_4$ (942.49): calcd. C 40.78 H 3.86 P 6.57 Rh 10.62 S 13.60; found C 40.15 H 3.96 P 6.60 Rh 10.28 S 13.10. – ^{31}P NMR (D_2O): δ 64.1 (d, $J_{Rh,P}$ = 160.0 Hz). – ^{19}F NMR (D_2O): δ –152.7.

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