New, Highly Efficient Work-Up Protocol for Sulfonated Diphosphines

Wilhelmus P. Mul,[a,*] Kevita Ramkisoensing,[b] Paul C. J. Kamer,[b,*] Joost N. H. Reek,[b] Arjan J. van der Linden,[a] Angelica Marson,[a] Piet W. N. M. van Leeuwen[b]

[a] Shell Research and Technology Centre, Amsterdam, P.O. Box 38000, 1030 BN Amsterdam, The Netherlands
E-mail: pim.mul@shell.com

[b] Institute of Molecular Chemistry, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands
Fax: (+31)-20-525-6422, e-mail: kamer@science.uva.nl

Received: November 8, 2001; Accepted: February 10, 2002

Abstract: Isolation of a series of sulfonated diphosphines via a new highly efficient method is described. The work-up procedure involves the precipitation of the sulfonated ligand prior to neutralization, and subsequent removal of the sulfuric acid by filtration and washing. Great advantages of this procedure are its simplicity and easiness to scale-up while co-production of large amounts of sulfate salts is avoided.

Keywords: aqueous biphasic catalysis; homogeneous catalysis; P-ligands; sulfonation

Introduction

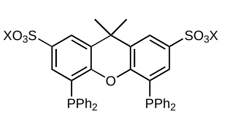
The reactivity of organotransition metal complexes is dependent on the ligand environment of the metal. Consequently, optimizing the performance of the catalytic center by varying the ligand properties is a powerful tool in homogeneous catalysis. Impressive results have been obtained in both small-scale (asymmetric) catalytic preparation of fine-chemicals and industrial production of bulk-chemicals.

Many successful homogeneous catalysts are based on ligands containing phosphorus donor atoms.[1] Especially phosphines have been applied in a plethora of selective catalytic transformations. The difficulty in separation of the homogeneous catalyst system from organic products, however, limits the application of homogeneous catalysis in the chemical industry. An elegant solution to this problem has been provided by the application of two-phase catalysis. This concept was first applied industrially in the Shell higher olefin process using a catalyst containing polar 1,4-butanediol phase and an apolar α-olefin product phase.[1] Other interesting concepts based on two-phase catalysis including those that make use of ionic liquids,[2] fluorous solvents,[3] or supercritical CO_2[4] suffer from high operational costs.

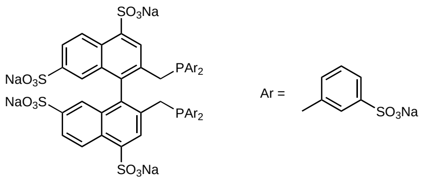
An elegant alternative is the use of water as a cheap, non-toxic, non-flammable, environmentally friendly polar solvent in a two-phase process. Aqueous-phase catalysis proved to be valuable as demonstrated by the success of the Ruhrchemie-Rhône Poulenc process, which is based on a rhodium-TPPTS catalyst for the hydroformylation of propene in water.[5] The great potential for industrial applications of two-phase catalysis has triggered the development of many new hydrophilic phosphines.[6]

Analogously to homogeneous catalysis in organic solvents highly selective, tailor-made water-soluble catalysts have been developed. Water-soluble bidentates like sulfoxantphos (**1**)[7] and BINAS (**2**)[8] gave similar excellent selectivities in the rhodium-catalyzed hydroformylation of alkenes as their organic counterparts,[9,10] while bdompp-S (**3**) outperforms its non-sulfonated counterpart in the palladium-catalyzed copolymerization of carbon monoxide and α-olefins.[11,12]

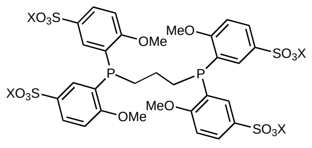
Despite the fact that high-performance catalysts are available, TPPTS is still the only water-soluble ligand that is industrially applied. The main reason is that application of a homogeneous catalyst at industrial scale requires the applied ligand system to be synthetically readily accessible. Most synthetic procedures for water-soluble ligands involve the use of fuming sulfuric acid (oleum) for sulfonation.[13] The vigorous reaction conditions result in side reactions like formation of phosphine oxides and laborious work-up methods are often required[13] An elegant alternative synthetic procedure, developed by Stelzer and coworkers, is the catalytic cross-coupling of phosphines and haloarylsulfonic acids.[14] This method, however, is not always successful for the preparation of sophisticated bidentate ligands. Most present purification methods have in common that they involve neutralization of the sulfuric acid solution of the sulfonated ligand, resulting in the formation of large amounts of sulfate salts. The purification proce-



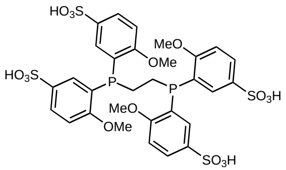
1a, X = H; **1b**, X = Na



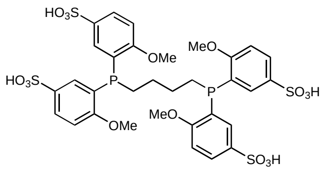
2



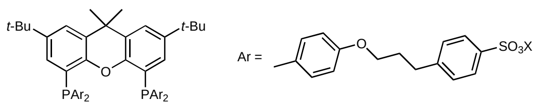
3a, X = H; **3b**, X = Na



4a



5a



6a, X = H; **6b**, X = Na

dures required to remove the salts comprise repeated fractional crystallization,[15] extraction and reextraction procedures,[16] or chromatographic techniques.[17] Isolation can be accomplished by extraction of the sulfonated phosphine from the hydrolyzed reaction mixture with a hydrophobic amine (e.g., tri-*iso*-octylamine) dissolved in toluene, followed by a sequence of neutralization – reextraction – neutralization steps.[16] Although co-production of sulfate salt is reduced considerably this way, it is not fully prevented, while contamination of the product with sulfate salt is not easy to avoid. These tedious procedures are difficult to perform on large scale. Careful adjustment of the reaction conditions, for instance, phosphine protection using boric acid, can improve the yield and selectivity of the sulfonation,[18] but the tedious purification steps remain. In addition, complications in the work-up procedure like gel-formation or precipitation of sticky solids have been reported.[19] The use of sodium oxalate or basic aluminum oxide has been reported to facilitate work-up and suppress phosphine oxidation.[20] Oxidation of TPPTS during work-up can also be substantially suppressed by careful control of the pH.[21]

Here we report a general work-up procedure that involves the precipitation of the sulfonated ligand prior to neutralization, and subsequent removal of the sulfuric acid by filtration and washing.[22] Some sulfonated analogues of diphosphines often used in catalysis were prepared as representative examples. Bis(diarylphosphines) containing both aliphatic, 1,2-bis[(di-(2-methoxy,5-sulfonatophenyl)phosphino]ethane (bdompe-S, **4**), and 1,4-bis[di-(2-methoxy,5-sulfonatophenyl)phosphino]butane (bdompb-S, **5**), and rigid (hetero)aromatic, sulfoxantphos (**1**) and **6**, linkers were prepared. A great advantage of this procedure is that it can be scaled up easily and the amounts of side products and salt formation are low.

Results and Discussion

The most widely used method to obtain water-soluble phosphines is the controlled sulfonation in fuming sulfuric acid.[13,23] This method can pose problems regarding the formation of side products like phosphine oxides. Also sulfonation is not always (regio-) selective and a mixture of sulfonated products is often obtained.

The diphosphines containing aliphatic bridges and activated triarylphosphine were sulfonated using sulfuric acid, whereas the triarylphosphine xantphos required the addition of oleum. Sulfonation was monitored by ^{1}H and ^{31}P NMR and complete and selective conversion of the diphosphines took place within 24 – 48 h. Formation of phosphine oxides was not observed when sulfuric acid was used, whereas the application of oleum resulted in small amounts of phosphine oxides. To minimize the amount of phosphine oxides the reactions using oleum were started and worked-up at low temperature.

Isolation of the sulfonated product, bdompb-S[H]$_4$ (**5a**) was achieved following the same procedure reported for the C$_3$-bridged analogue, bdompp-S (**3a**).[12] After stirring bdompb and concentrated sulfuric acid for 24 h at ambient temperature, the pale orange solution was hydrolyzed with a 5-fold (v/v) excess of water, whilst keeping the temperature below 20 °C, resulting in the immediate precipitation of a white microcrystalline solid. After storage of the mixture at –20 °C for one day, bdompb-S[H]$_4 \cdot 8$ H$_2$O **5a** (elemental analysis) was isolated as a pure product in high yield (91%) after filtration and washing with butanone and diethyl ether. The residual sulfuric acid content was about 0.5 wt %.

The reaction of the C$_2$-bridged bdompe with sulfuric acid resulted in an unexpected dark green solution. Sulfonation was followed by ^{31}P NMR and was completed within 48 h. When the reaction mixture was hydrolyzed, cooling resulted in precipitation of a tiny amount of a fine green powder, which was further discarded. Only after removal of the green contaminant by filtration over Celite, did storage of the thus obtained colorless solution at –20 °C result in the formation of a white precipitate in substantial amount. The pure product, bdompe-S[H]$_4 \cdot 4$ H$_2$O (**4a**) was obtained in good yield (65%) after filtration, washing with butanone and diethyl ether, and drying.

The sulfonation of 9,9-dimethyl-4,5-bis(diphenylphosphino)xanthene gave a high yield of **1a** when the reaction conditions were carefully controlled.[7] 9,9-Dimethyl-4,5-bis(diphenylphosphino)xanthene was dissolved in concentrated sulfuric acid to prevent oxidation of the phosphines by protection as phosphonium salt after protonation. In this way the addition of oleum to the reaction mixture at 0 °C did not lead to oxidation. In order to assure complete sulfonation the reaction mixture was stirred at room temperature for 24 h. After cooling the viscous red reaction mixture to – 10 °C, water was added slowly and carefully to dilute the reaction mixture. This resulted in immediate precipitation of a sticky white solid. After filtration, washing with ethyl acetate and drying, the acidic product was obtained as a white powder. The sodium salt (**1b**) could be prepared by dissolving the solid material in an aqueous 0.5 M NaOH solution that contained exactly 2 equivalents of NaOH, and subsequent removal of the water by freeze-drying.

In general, sulfonation of triarylphosphines is troublesome because under the reaction conditions the protonated phosphine is a strong electron-withdrawing group, which slows down the electrophilic aromatic substitution. An elegant procedure to overcome this problem has been developed by Hanson et al.[24,25] They substituted the arylphosphine with a second phenyl separated by a bridge of aliphatic carbon atoms. The second aromatic ring is activated at the 4-position and the obtained product has an amphiphilic character. We previously applied this technique for the preparation of xantphos-type ligands, which resulted in the preparation of amphiphilic diphosphines **6.**[26] Here, we use a similar sulfonation procedure, which now includes a precipitation step in the work-up method.

The reaction conditions were carefully controlled to prevent formation of side-products. Because of solubility problems, the starting material was dissolved in dichloromethane and sulfuric acid was added at –90 °C. The dichloromethane was removed under vacuum whilst warming to room temperature. In order to assure complete sulfonation, the reaction mixture was stirred at room temperature for 5 days and the reaction was followed by NMR spectroscopy. After careful addition of water at –10 °C, a white sticky solid precipitated immediately. After filtration, washing with ethyl acetate, and drying, the acidic product was obtained as a white powder. The sodium salt (**6b**) could be prepared by dissolving the solid material in an aqueous 0.5 M NaOH solution that contained exactly 4 equivalents of NaOH, and subsequent removal of the water by freeze-drying.

The sulfonated products (**1, 4 – 6**) were precipitated by mixing (***caution***) the reaction mixture with a controlled amount of water, followed by cooling if required.[27] Subsequently, the products were isolated as white powders by filtration, washing and drying. The amount of aqueous sulfuric acid attached to the crude products should be kept as low as possible, otherwise gel-formation may occur during washing. During washing it is of importance to remove the sulfuric acid remainders efficiently, otherwise neutralization of the sulfonic acid groups, by addition of a stoichiometric amount of NaOH in a next step, will not be complete and will be accompanied by formation of salt (Na_2SO_4, $NaHSO_4$). We found that, depending on the structure of the product, different solvents are required to wash the products smoothly. In general, solvents of medium polarity like acetone, butanone and ethyl acetate are most suitable. The use of more polar solvents like ethanol and *iso*-propanol may lead to the formation of a gel during work-up. The products can be isolated as pure (hydrated) acids (**1a, 4 – 6a**) or, after neutralization of the sulfonic acid groups by sodium hydroxide, as sodium sulfonates (exemplified for **1b** and **6b**). Both forms can be used to prepare catalysts from transition metal precursors.

It has been reported that isolation of bdompp-S[H_4] (**3a**) via the same precipitation procedure as discussed here, affords the product in acidic, hydrated form.[12] X-ray crystal structure analysis and ^{31}P NMR indicated **3a** to exist as a bis-zwitterionic species, containing two protonated phosphorus atoms, both in the solid state and in aqueous solution. The sulfonated products **4a** and **5a** were also isolated in acidic, hydrated form (containing 4 or 8 molecules of water per molecule of product) and were characterized in solution by ^{1}H and ^{31}P NMR, confirming the occurrence of sulfonation exclusively in the *para* position with respect to the *o*-methoxy substituents. No signals due to the formation of phosphine oxides or other by-products were detected.

Regarding the signals displayed in ^{31}P NMR, a large difference in chemical shift was found between the two sulfonated diphosphines. For the bdompb-S[H]$_4$ (**5a**) a sharp singlet was found at – 0.48 ppm in D_2O, while for bdompe-S[H]$_4$ (**4a**) the resonance was broad (a high concentration of the product is necessary to obtain a clear spectrum) and highly up-field shifted (– 9.43 ppm). This prompted us to investigate the effect of a strong acid on the position of these signals. Addition of small aliquots of hydrochloric acid to an aqueous solution of bdompe-S[H]$_4$ resulted in a progressive down-field shift of the singlet, reaching a highest value of 0.51 ppm, and in a gradual sharpening of this resonance. In contrast, the ^{31}P resonance for bdompp-S[H]$_4$ (**3a**) and bdompb-S[H]$_4$ (**5a**) are virtually unaffected by variation of the acidity. Based on these results, we propose that bdompe-S[H]$_4$ occurs in two forms, mono- (**4a**) and bis-protonated (**4a'**, see Figure 1), that can be interconverted by changing the acid concentration.

It is proposed that upon increasing the acidity of the solution, **4a**, which contains a bridging proton in a relatively stable five-membered ring, is converted into **4a'**, containing a proton on each phosphorus atom. This equilibrium does not seem to occur for bdompp-S[H]$_4$

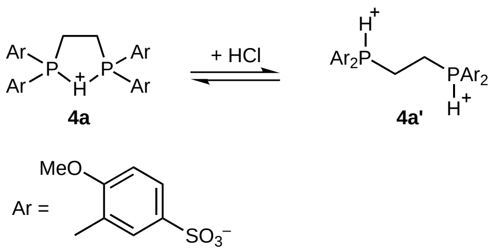


Figure 1. Acid dependent equilibrium of compound **4a.**

and bdompb-S[H]$_4$, most likely because the corresponding 6- and 7-membered rings are less favorable resulting in protonation of both phosphorus atoms.

The water content of the sulfonated phosphine products was determined by elemental analysis. The products **4a** and **5a** contained about 4 or 8 molecules of water, respectively, per molecule of sulfonated diphosphine. The sulfuric acid content in the product was determined with the aid of ion chromatography, analyzing for sulfate anions. After optimization of the work-up procedure and application of a suitable washing solvent, the residual amount of sulfuric acid did generally not exceed 1.0 wt %.

The acidic products **1a** and **6a** were isolated and were characterized by ^{1}H and ^{31}P NMR in CD_3OD. The signals in the ^{31}P NMR spectra are shifted downfield compared to the sodium salts. For **1a**, a sharp singlet was found at –10.92 ppm and a broad ^{31}P NMR resonance was observed for **6a** at –4.8 ppm. According to ^{1}H NMR of **1**, the sulfonate groups are positioned exclusively on the xanthene backbone *meta* to the phosphorus atoms and *para* to the oxygen atom as indicated by two singlet signals in the aromatic region for the aromatic protons on the xanthene backbone. No sulfonation of the C_6H_5 substituents on phosphorus was observed.

Conclusion

In conclusion, we have developed a new, straightforward and highly efficient procedure for the isolation of sulfonated diphosphines. Application of this procedure avoids the undesired co-production of sodium sulfate as chemical waste and, more importantly, simplifies work-up considerably. Since this method does not require complicated consecutive extraction or crystallization steps it can easily be scaled up for industrial purposes. It is expected that this procedure is applicable for a broad range of sulfonated (di)phosphines.

Experimental Section

General Procedures

All reactions and measurements were carried out using standard Schlenk techniques under an atmosphere of argon or purified nitrogen. Methanol and dichloromethane were distilled from CaH_2 under nitrogen prior to use. Concentrated sulfuric acid (96%) and oleum (65%) were purchased from Merck or Aldrich Chemical Co. All chemicals were used without further purification. 1,2-Bis[di-(2-methoxyphenyl)-phosphino]ethane (bdompe),[28] 1,4-bis[di-(2-methoxyphenyl)phosphino]butane (bdompb),[29] 9,9-dimethyl-4,5-bis(diphenylphosphino)xanthene,[7] and 2,7-di-*tert*-butyl-4,5-bis{-di[*p*-(3-phenylpropyl)phenoxy]-phosphino}-9,9-dimethylxanthene[26] were prepared according to literature methods. ^{1}H, ^{13}C and ^{31}P{^{1}H} NMR spectra were recorded using the following spectrometers: Varian Mercury 300, Varian GEMINI-300, Varian INOVA-400 and Varian Inova 500. The ^{1}H and ^{13}C chemical shifts are given in ppm relative to TMS and the ^{31}P chemical shifts are given in ppm relative to 85% H_3PO_4.

The sulfate content of the sulfonated diphosphines was determined by ion chromatography (IC) against a standard sulfate solution. Conditions: DX100 (DIONEX), measured area (analogous) 0 – 1000 μS; column: AG9 (guard column) and AS4SC (separation column); eluent: 1.5 mM HCO_3^-/ 1.2 mM CO_3^{2-} demineralized water. Detection was achieved conductometrically. Elemental analyses were performed by 'Analytische Laboratorien', Lindlar (Germany).

Bdompe-S[H]$_4$ · 4 H_2O (4a)

Bdompe (0.90 g, 1.73 mmol) was added in small portions to 8 g of concentrated sulfuric acid (95 – 97%) whilst cooling the reaction mixture on ice. The sulfonation reaction was monitored by ^{1}H NMR. The dark green solution was stirred for 24 h at ambient temperature and, after addition of 3 g of sulfuric acid (incomplete reaction), for an additional 24 h. The solution was poured slowly into 31 mL of water at 0 °C and filtered over Celite® to remove a green component. After storage of the filtrate for one week at –20 °C a white precipitate was formed which was isolated by filtration, and washed with four portions of butanone (10 mL each) and one portion of diethyl ether (10 mL). After drying for 3 h at 55 °C under vacuum, bdompe-S[H]$_4$ · 4 H_2O was obtained; yield: 0.95 g (65%). ^{1}H NMR (400 MHz, D_2O): $\delta = 7.78$ (dd, $J = 8.8$, $J = 2.3$ Hz, 4H, H-4), 7.63 (m, 4H, H-6), 6.90 (ddd, $J = 8.8$, $J = 2.4$, $J = 2.3$ Hz, 4H, H-3), 3.52 (s, 12H, $O\underline{CH_3}$), 2.69 (m, 4H, $\underline{CH_2}P$); ^{31}P NMR (121.5 MHz, D_2O): $\delta = -9.43$; ^{13}C NMR (100.6 MHz, D_2O): $\delta = 163.2$ (s, C-2), 136.4 (m, C-5), 132.9 (s, C-4), 131.8 (m, C-6), 112.4 (s, C-3), 111.3 (m, C-1), 56.5 (s, $O\underline{CH_3}$), 15.5 (m, $\underline{CH_2}P$); anal. found/(calcd.) for $C_{30}H_{40}P_2S_4O_{20}$: C 39.23/(39.56), H 4.43/(4.43), P 6.39/(6.80), S 14.18/(14.08); H_2SO_4 content (IC): 0.56 wt %.

Bdompb-S[H]$_4$ · 8 H_2O (5a)

Bdompb (0.90 g, 1.65 mmol) was added in small portions to 8 g of sulfuric acid whilst cooling the reaction mixture on ice. The pale orange solution was stirred for additional 24 hours, whilst monitoring the sulfonation by ^{1}H NMR and then was poured slowly in 23 mL of water at 0 °C. After storage at –20 °C for one day a white precipitate was formed which was isolated by filtration and was washed with four portions of 10 mL of butanone and one portion of 10 mL of diethyl ether. After drying for 3 h at 55 °C under vacuum, bdompb-S[H]$_4$ · 8 H_2O was obtained; yield: 1.30 g (91%);of ^{1}H NMR (400 MHz, D_2O): $\delta = 7.94$ (dd, $J = 8.8$, $J = 2.3$, 4H, H-4), 7.88 (m, 4H, H-6), 7.11 (dd, $J_{PH} = 5.7$, J = 8.8 Hz, 4H, H-3), 3.68 (s, 12H, $O\underline{CH_3}$), 2.81 (m, 4H, $CH_2\underline{CH_2}P$), 1.60 (m, 4H, $\underline{CH_2}CH_2P$); ^{31}P NMR (121.5 MHz, D_2O): $\delta = -0.48$; ^{13}C NMR (100.6 MHz, D_2O): $\delta = 163.5$ (s, C-2), 136.8 (d, C-5), 135.1 (s, C-4), 132.1 (d, C-6), 113.0 (d, C-3), 104.3 (d, C-1), 57.0 (s, $O\underline{CH_3}$), 23.5 (d, $\underline{CH_2}CH_2$ P), 17.0 (d, $CH_2\underline{CH_2}P$); anal. found/(calcd.) for $C_{32}H_{52}P_2S_4O_{24}$: C 38.09/(38.02), H 5.00/(5.18), P 6.19(6.13), S 12.79/(12.69); H_2 SO_4 content (IC): 1.0 wt %.

9,9-Dimethyl-4,5-bis(diphenylphosphino)xanthene-2,7-bissulfonic Acid (1a)

A solution of 9,9-dimethyl-4,5-bis(diphenylphosphino)xanthene (1.02 g, 1.76 mmol) in dry dichloromethane (3 mL) was cooled to 0 °C and concentrated sulfuric acid (1.5 mL) was added. Dichloromethane was removed by evaporation under vacuum, and after 9,9-dimethyl-4,5-bis(diphenylphosphine) xanthene was completely dissolved in the concentrated sulfuric acid, oleum (1.5 mL) was added to the cooled solution. Subsequently the mixture was warmed to room temperature and stirred for 24 h. After cooling the reaction mixture to –10 °C, degassed ice/water (8 mL) was added slowly to the solution, which resulted in a white precipitate (***caution:*** this reverse addition must be performed at low temperature to avoid splashing of acid). After filtration, the white solid was washed twice with ethyl acetate (2′ 4 mL). After drying at 70 °C under vacuum crude **1a** was obtained; yield: 1.26 g; ^{1}H NMR (CD_3OD): $\delta = 8.07$ (s, 2H), 7.36 – 7.26 (m, 22H), 1.68 (s, 6H); ^{31}P NMR (CD_3OD): $\delta = -10.92$ (s). The crude product was used for the synthesis of **1b** without further purification

9,9-Dimethyl-2,7-bissulfonato-4,5-bis(diphenylphosphino)xanthene Sodium Salt (1b)

Compound **1a** (0.96 g) was neutralized with a 0.5 M NaOH solution (5.2 mL) in water and the water was removed by freeze-drying. The product was washed with EtOH (7 mL) and a white powder was obtained; yield: 0.90 g (88%); ^{1}H NMR (CD_3OD): $\delta = 8.00$ (s, 2H), 7.28 – 7.18 (m, 22H), 1.69 (s, 6H); ^{31}P NMR (CD_3OD): $\delta = -12.8$ (s) (lit.[7] $\delta = -14.7$).

2,7-Di-*tert*-butyl-9,9-dimethyl-4,5-bis{di[*p*-(3-*p*-sulfonic acid)phenylpropyl)phenoxy]phosphino}xanthene (6a)

A solution containing 2,7-di-*tert*-butyl-9,9-dimethyl-4,5-bis {di[*p*-(3-phenylpropyl)phenoxy]phosphino}xanthene (1.00 g, 0.81 mmol) in dry dichloromethane (5 mL) was cooled to –90 °C and concentrated sulfuric acid (2 mL) was added. Dichloromethane was removed under vacuum while the reaction mixture was slowly warmed to room temperature. Subsequently the reaction mixture was placed under argon and stirred for 5 days. After cooling the reaction mixture to –10 °C, degassed ice water (7 mL) was added slowly to the solution, which resulted in a white precipitate (***caution:*** this reverse addition must be performed at low temperature to avoid splashing of acid). After filtration, the white solid was washed twice with ethyl acetate (2 ’ 4 mL). After drying at 70 °C under vacuum crude **6a** was obtained as an off-white powder; yield: 0.79 g; ^{1}H NMR (CD_3OD): $\delta = 7.76$ (d, $J = 8$ Hz, 8H), 7.31 (d, $J = 8$ Hz, 8H), 7.31 – 7.06 (m, 10H), 7.00 (dd, $^1J = 8.5$ Hz, $^2J = 2.0$ Hz, 8H), 6.75 (dd, $^1J = 16$ Hz, $^2J = 2.0$ Hz, 2H), 4.07 (t, $J = 7.0$ Hz, 8H), 2.86 (t, $J = 7.5$ Hz, 8H), 2.12 (t, $J = 7$ Hz, 8H), 1.82 (s, 6H), 1.18 (s, 18H); ^{31}P NMR (CD_3OD) $\delta = -4.8$ (br s). The crude product was used for the synthesis of **6b** without further purification.

2,7-Di-*tert*-butyl-9,9-dimethyl-4,5-bis{di[*p*-(3-*p*-sulfonatophenylpropyl)phenoxy]phosphino}xanthene Sodium Salt (6b)

The acidic product **6a** (0.60 g) was neutralized using a 0.5 M NaOH solution (2.89 mL) and the water was removed by freeze-drying. The phosphine oxide formed during the synthesis of **6a** was removed by washing with EtOH (4.5 mL), and after drying in vacuum a white powder was obtained; yield: 0.46 g (76%); ^{1}H NMR (CD_3OD): $\delta = 7.72$ (d, $J = 8.3$ Hz, 8H), 7.44 (s, 2H), 7.28 (d, $J = 8.3$ Hz, 8H), 7.04 (br, 8H), 6.81 (d, $J = 8.6$ Hz, 8H), 6.55 (s, 2H), 3.95 (t, $J = 6.2$ Hz, 8H), 2.84 (t, $J = 7.3$ Hz, 8H), 2.08 (m, 8H), 1.63 (s, 6H), 1.12 (s, 18H); ^{31}P NMR (CD_3OD) $\delta = -15.09$ (br s) (lit.[26] $\delta = -15.4$).

Acknowledgements

We thank A. B. van Oort for technical assistance. The Netherlands foundation for Chemical Research (CW) and the Netherlands Organization for Scientific Research (NWO) are acknowledged for financial support and Shell International Chemicals B.V. for giving permission to publish this paper.

References and Notes

[1] a) P. W. Glockner, W. Keim, R. F. Mason, R. S. Bauer, (to Shell), *DE* 2,053,758, **1971**; *Chem. Abstr.* **1971**, *75*, 88072; b) W. Keim, *Chem. Ing. Tech.* **1984**, *56*, 850.

[2] a) T. Welton, *Chem. Rev.* **1999**, *99*, 2071; b) P. Wasserscheid, W. Keim, *Angew. Chem. Int. Ed.* **2000**, *39*, 3773.

[3] I. T. Horváth, J. Rábai, *Science* **1994**, *266*, 72.

[4] a) P. G. Jessop , T. Ikariya , R. Noyori, *Chem. Rev.* **1999**, *99*, 475; b) J. A. Darr, M. Poliakoff, *Chem. Rev.* **1999**, *99*, 495.

[5] E. G. Kuntz, *Chemtech* **1987**, *17*, 570.

[6] B. Cornils, W. A. Herrmann, *Aqueous Phase Organometallic Catalysis, Concepts and Applications*, VCH, Weinheim; New York, Basel, Cambridge, Tokyo, **1998**.

[7] M. Schreuder Goedheijt, P. C. J. Kamer, P. W. N. M. van Leeuwen, *J. Mol. Catal. A Chem.* **1998**, *134*, 243.

[8] a) W. A. Herrmann, C. W. Kohlpaintner, R. B. Manetsberger, H. Bahrmann, H. Kottmann, *J. Mol. Catal.* **1995**,

97, 65; b) H. Bahrmann, K. Bergrath, H.-J. Kleiner, P. Lappe, C. Naumann, D. Peters, K. Regnat, *J. Organmet. Chem*. **1996**, *520*, 97.

[9] M. Kranenburg, Y. E. M. van der Burgt, P. C. J. Kamer, P. W. N. M. van Leeuwen, K. Goubitz, J. Fraanje, *Organometallics* **1995**, *14*, 3081.

[10] a) K. Tamao, H. Yamamoto, H. Matsumoto, N. Miyake, T. Hayashi, M. Kumada, *Tetrahedron Lett*. **1977**, *16*, 1389; b) T. J. Devon, G. W. Phillips, T. A. Puckette, J. L. Stavinoha, J. J. Vanderbilt, (to Texas Eastman), *U. S. Patent* 4,694,109, **1987**; *Chem. Abstr.* **1988**, *108*, 7890.

[11] G. Verspui, G. Papadogianakis, R. A. Sheldon, *Angew. Chem. Int. Ed.* **2000**, *39*, 804.

[12] W. P. Mul, H. Dirkzwager, A. A. Broekhuis, H. J. Heeres, A. J. van der Linden, A. G. Orpen, *Inorg. Chim. Acta* **2002**, *327*, 147.

[13] W. A. Hermann, C. W. Kohlpaintner, *Angew. Chem. Int. Ed.* **1993**, *32*, 1524.

[14] O. Herd, A. Heßler, M. Hingst, M. Tepper, O. Stelzer, *J. Organomet. Chem*. **1996**, *522*, 69.

[15] B. Cornils, E. G. Kuntz *J. Organomet. Chem.* **1995**, *502*, 177.

[16] W. A. Herrmann, C. W. Kohlpaintner, H. Bahrmann, W. Konkol *J. Mol. Catal. A Chem.* **1992**, *73*, 191.

[17] a) L. Lecomte, J. Triolet, D. Sinou, *J. Chromatogr.* **1987**, *408*, 416; b) W. A. Herrmann, J. A. Kulpe, W. Konkol, H. Bahrmann, *J. Organomet. Chem*. **1990**, *389*, 85.

[18] W. A. Herrmann, G. P. Albanese, R. B. Manetsberger, P. Lappe, H. Bahrmann, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 811.

[19] A. E. Sollewijn Gelpke, J. J. N. Veerman, M. Schreuder Goedheijt, P. C. J. Kamer, P. W. N. M. van Leeuwen, H. Hiemstra *Tetrahedron* **1999**, *55*, 6657.

[20] H. Jänsch, S. Kannenberg, G. Boche, *Eur. J. Org. Chem.* **2001**, 2923.

[21] S. Hida, P. J. Roman Jr., A. A. Bowden, J. D. Atwood, *J. Coord. Chem.* **1998**, *43*, 345.

[22] As an early example the sulfonated diphosphine 1,3-bis[di-(2-methoxy-5-sulfonato-phenyl)phosphino]propane, (bdompp-S) was previously isolated using this method, see Ref.[12]

[23] P. Kalck, F. Monteil, *Adv. Organomet. Chem*. **1992**, *34*, 219.

[24] H. Ding, B. E. Hanson, J. Bakos, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1645.

[25] H. Ding, B. E. Hanson, T. Bartik, B. Bartik *Organometallics* **1994**, *13*, 3761.

[26] M. Schreuder Goedheijt, B. E. Hanson, J. N. H. Reek, P. C. J. Kamer, P. W. N. M. van Leeuwen, *J. Am. Chem. Soc.* **2000**, *122*, 1650–1657.

[27] A broad range of water:sulfuric acid ratios could be applied; high product yields were obtained over the range of 2:1 – 10:1 (v/v).

[28] I. M. Angulo, E. Bouwman, M. Lutz, W. P. Mul, A. L. Spek, *Inorg. Chem*. **2001**, *40*, 2073.

[29] P. H. M. Budzelaar, J. A. van Doorn, N. Meijboom, *Recl. Trav. Chim. Pays-Bas* **1991**, *110*, 420.