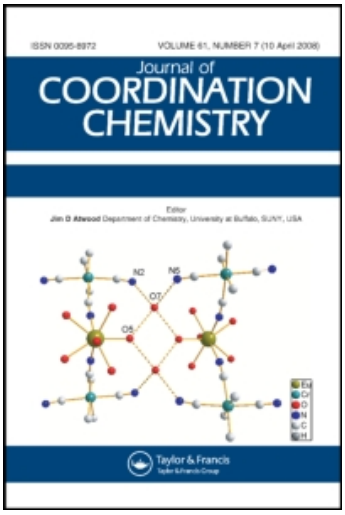


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# Synthesis of tri(*m*-sulfonatedphenyl)phosphine (tppts): The importance of ph in the work-up

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# SYNTHESIS OF TRI(*m*-SULFONATEDPHENYL)PHOSPHINE (TPPTS): THE IMPORTANCE OF pH IN THE WORK-UP

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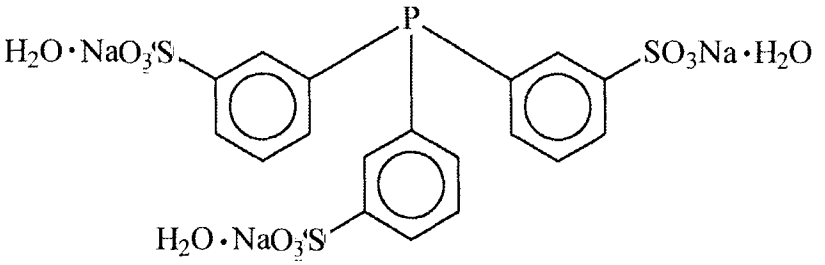
Controlling the pH during workup allows synthesis of TPPTS, P(*m*-$C_6H_4SO_3Na)_3$, without interference from the oxide. The recrystallized yield is 70% based on P(*m*-$C_6H_4SO_3Na)_3 \cdot 3H_2O$ from $PPh_3$.

*Keywords:* TPPTS; water soluble; sulfonated ligands

The ligand TPPTS (P(*m*-$C_6H_4SO_3Na)_3$) is the center of the Rhoñe-Poulenc hydroformylation process [1] and the most important ligand for studies of organometallic complexes in aqueous solution.[2-4] Its synthesis was published in the patent literature,[5] but has proven difficult to reproduce due to phosphine oxide formation.[1b, 6] A new synthesis of TPPTS was developed using a

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sulfuric acid/boric acid mixture with reported decreased oxidation product.[6] In this communication we report that the synthesis of TPPTS can be effected by the original procedure with the amount of oxide controlled by the pH of the work-up.

A 1,000 ml three-neck round bottom flask is equipped with a stir bar and flushed with $N_2$(g) for 15 mins, followed by addition of 50 mL fuming sulfuric acid. The flask is then cooled with an ice bath for 30 mins and 5g (0.019 mole) of triphenylphosphine added under $N_2$(g) purge; this addition should take at least one hour. Once the phosphine is in solution the flask is sealed and stirred in a $N_2$(g) atmosphere for 7 days at room temperature and then for 5 days at 5°C. Next the pH of the solution is adjusted to around 3 by adding deaerated 20% NaOH using a dropping funnel. This should take 90 mins and be carried out in an ice bath. The volume is then reduced to 100 mL by distillation under $N_2$(g). Sodium sulfate is precipitated from the solution by addition of 500 mL of deaerated methanol, followed by 30 mins reflux. The solid is separated by vacuum filtration and washed with 250 mL of hot deaerated methanol. Filtrate and washings are transferred to a 1,000 mL round bottom flask and the volume reduced to 100 mL *in vacuo*. This is then flushed with $N_2$(g) for 15 min and 500 mL of deaerated acetone added to precipitate the trisulfonated phosphine. Vacuum filtration of the white precipitate allows the product to be isolated as a mixture of the phosphine oxide and desired product. The oxide is present at around 5%. The yield, based on TPPTS trihydrate, is 70%. The NMR characterization data (a single $^{31}$P resonance at −4.3 ppm (DMSO) and −5.1 ppm ($D_2O$)) are consistent with those previously reported[4] and the analytical data confirm the purity: $P(C_6H_4SO_3Na)_3 \cdot 3H_2O$, *Anal. calcd.* for $C_{18}H_{18}Na_3O_{12}PS_3$ (%): C, 34.73; H, 2.91; Na, 11.08; S, 15.45; P, 4.98. Found: C, 34.66; H, 3.03; Na, 11.24; S, 15.68; P, 4.76.

If required, the oxide may then be removed by extraction using a deaerated mixture of acetone, methanol and water (in a 10:5:1 ratio).[4] This is added under $N_2$, the solution filtered, the resulting solid dissolved in 75 mL of deaerated water, and precipitated by addition of 500 mL of deaerated acetone.

The original procedure for sulfonation of $PPh_3$ with fuming sulfuric acid calls for neutralization of the sulfuric acid, but gives no indication of the importance of pH. At low pH's the phosphine is protected from oxidation by protonation to the phosphonium, $HPR_3^+$. This is essential given the strongly oxidizing character of the fuming sulfuric acid. A brief report suggested that TPPTS could not be protonated.[7] Studies of $PPh_3$ indicate a $pK_a$ of 2.73;[8, 9] substituents on the phenyl ring changed the $pK_a$ somewhat, but the phosphorus would be protonated at low pH. The meta sulfonation of the phenyl ring indicates that a phosphonium exists during the preparation of TPPTS. Thus protection from oxidation by

protonation seems reasonable. Neutralization converts the sulfonic acid complex into the more desirable water-soluble sodium salt.

$$HP(m\text{-}C_6H_4SO_3H)_3^{\ddagger} \xrightarrow{NaOH} HP(m\text{-}C_6H_4SO_3Na)_3^{\ddagger} \quad (1)$$

The sulfonic acid is deprotonated about pH = 1; to retain the protecting protonation of the phosphorus the pH needs to be less than 5.[8, 9]

The amount of oxide formed is quite dependent on pH. At pH's > 7 the amount of oxide can be ~95%; this is usually the pH that neutralization with NaOH gives. At pH = 4.5 the mixture contains significant quantities of $OPR_3$ and $PR_3$ and at pH = 2.5, 95% $PR_3$ was formed. $^{31}P$ NMR spectra of the same synthesis worked up at the different pH's are shown in Figure 1. The very different ratios

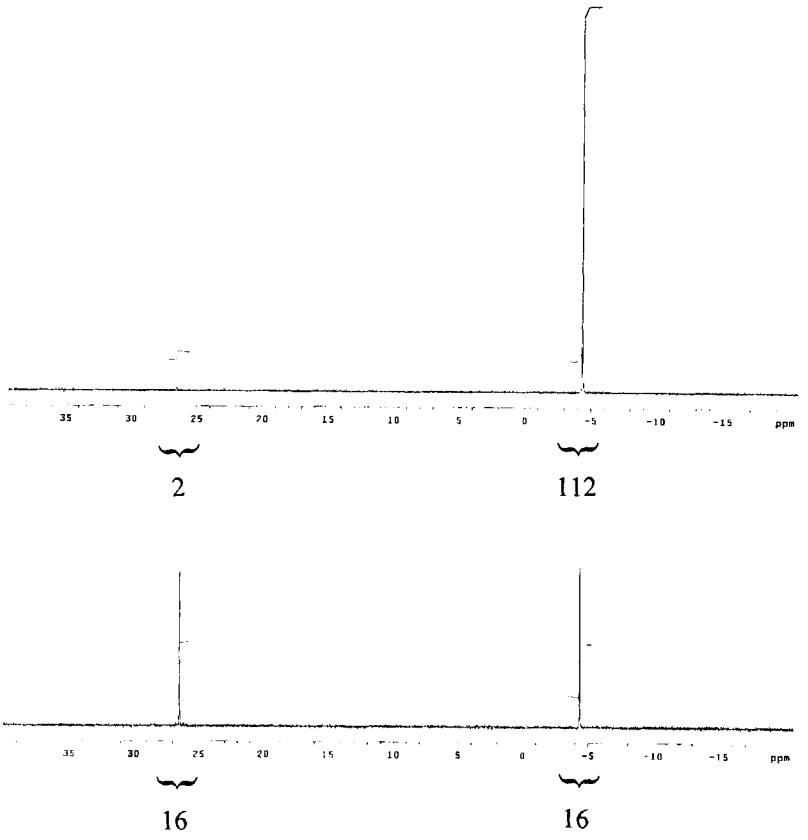


FIGURE 1 $^{31}P$ spectra of TPPTS and its oxide after splitting a reaction in half and working up the product at pH = 2.6 (top) and pH = 8 (bottom). The −4.4 ppm resonance is TPPTS and the 26.6 ppm resonance is the oxide of TPPTS.

of TPPTS to TPPTS oxide from the same synthesis show that oxide formation occurs during the reaction work-up, not during the synthesis. During neutralization at higher pH's $HP(m\text{-}C_6H_4SO_3H)_3^+$ is converted to $P(m\text{-}C_6H_4Na)_3$ which is susceptible to oxidation. By controlling the pH between 2 and 4 the phosphorus remains protonated while the sulfonic acid is deprotonated giving $HP(m\text{-}C_6H_4SO_3Na)_3^+$ which is still protected from oxidation. Thus as the pH increases the sequence shown in reaction 2 occurs. The reaction mixture with only 5% TPPTS oxide can be easily recrystallized to give analytically pure TPPTS.[4]

$$\begin{aligned} &HP(m\text{-}C_6H_4SO_3H)_3^+ \sim \underset{\rightarrow}{pH} \quad = 2\ HP(m\text{-}C_6H_4SO_3Na)_3^+ \\ &\quad pH \underset{\rightarrow}{=} 5\ P(m\text{-}C_6H_4SO_3Na)_3 \downarrow OP(m\text{-}C_6H_4SO_3Na)_3 \end{aligned} \tag{2}$$

The revised synthesis of TPPTS provides a convenient, reliable route to pure TPPTS and should increase the range of complexes to be examined in $H_2O$.



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### *References*

[1] (a) E. G. Kuntz, *Chem. Tech.*, 520 (1987) and references therein. (b) W. A. Herrmann and C. W. Kohlpaintner, *Angew. Chem. Int. Ed. Engl.*, **32**, 1524 (1993).
[2] (a) P. Kalck and F. Monteil, *Adv. Organomet. Chem.*, **34**, 219 (1992). (b) M. Barton and J. D. Atwood, *J. Coord. Chem.*, **24**, 43 (1991). (c) W. A. Herrmann, J. A. Kulpe, J. Kellner, H. Riepl, H. Bahrmann and W. Konkal, *Angew. Chem. Int. Ed. Engl.*, **29**, 391 (1990).
[3] E. Fache, C. Santini, F. Senocq and J. M. Basset, *J. Mol. Catal.*, **72**, 331 (1992).
[4] T. Bartik, B. Bartik, B. E. Hanson, T. Glass and W. Belont, *Inorg. Chem.*, **31**, 2667 (1992).
[5] E. G. Kuntz, French Patent 2314910, 20. 06, Rhône-Poulenc 1975.
[6] W. A. Herrmann, G. P. Albanese, R. B. Manetsberger, P. Lappe and H. Bahrmann, *Angew. Chem. Int. Ed. Engl.*, **34**, 811 (1995).
[7] T. Bartik, B. Bartik, B. E. Hanson, I. Guo and I. Tóth, *Organometallics*, **12**, 164 (1993).
[8] R. C. Bush and R. J. Angelici, *Inorg. Chem.*, **27**, 681 (1988).
[9] (a) C. A. Streuli, *Anal. Chem.*, **32**, 985 (1960). (b) T. Allman and R. G. Goel, *Can. J. Chem.*, **60**, 716 (1982).