



Pergamon

Tetrahedron Letters 41 (2000) 4503–4505

TETRAHEDRON
LETTERS

A practical synthesis of a disulfonated phosphine and its application to biphasic catalysis

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Received 16 March 2000; accepted 20 April 2000

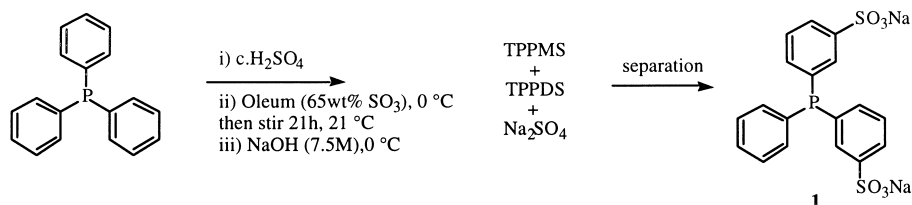
Abstract

A convenient synthesis of TPPDS (disodium P-phenyl-3,3'-phosphinediyl-bis(benzenesulfonate)) from triphenylphosphine is described. This represents a quick and reliable way to prepare a water-soluble phosphine with essentially no phosphine oxide formation. © 2000 Published by Elsevier Science Ltd.

Complexes of water-soluble phosphines have attracted considerable interest since the development of the Ruhrchemie/Rhône-Poulenc biphasic hydroformylation process.¹ TPPTS [P(*m*-C₆H₄SO₃Na)₃] was utilised in this process and is the most commonly used phosphine ligand for the preparation of water-soluble organometallic complexes.² The preparation of TPPTS is not trivial; this is demonstrated by the number of communications for its synthesis.³ Often the synthetic procedures are cumbersome and difficult to reproduce because of the formation of phosphine oxide during the reaction. Herein, we report on the synthesis of TPPDS [(C₆H₅)P(*m*-C₆H₄SO₃Na)₂] **1**, a water-soluble phosphine that can be prepared without the formation of phosphine oxide (Scheme 1). The procedure is straightforward, quick and reliable.

Triphenylphosphine⁴ (3.0 g, 11.4 mmol) and concentrated sulfuric acid (21 cm³) were placed in a 500 cm³ round-bottomed flask and stirred at room temperature until dissolution.⁵ The solution was then cooled to 0°C before the slow addition of oleum (9.5 cm³, 65 wt% SO₃). The flask was then sealed and the mixture stirred at room temperature for 21 hours. The neutralisation was carried out at 0°C by the slow, dropwise addition of NaOH (157 cm³, 7.5 M).⁶ The mixture, now containing crystalline sodium sulfate was then transferred to a 1000 cm³ round-bottomed flask

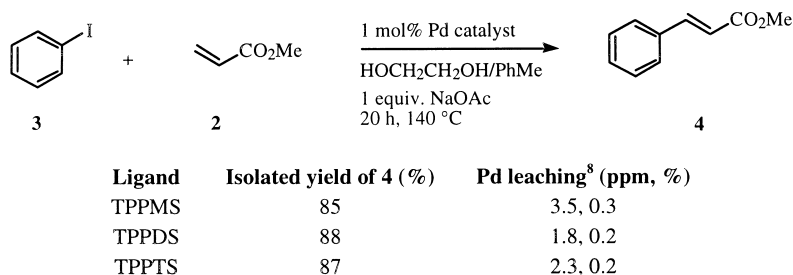
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Scheme 1.

and most of the water removed under vacuum. The remaining solid was refluxed in methanol (300 cm³) for 30 min and the solution filtered hot to remove the sodium sulfate. The methanol and residual water were removed under vacuum yielding a white solid. Dissolution of this solid in hot methanol (300 cm³) followed by the addition of ethyl acetate (850 cm³) caused the precipitation of TPPDS·2H₂O on standing. Yield: 3.45 g (60%).

The utility of TPPDS is demonstrated in a biphasic palladium-catalysed Heck reaction.⁷ TPPTS and TPPMS [(C₆H₅)₂P(*m*-C₆H₄SO₃Na)] were also used for comparison. Methyl acrylate **2** and iodobenzene **3** were treated with the prepared palladium catalyst in the presence of sodium acetate (Scheme 2).



Scheme 2.

The results show that each catalyst is effective in the formation of methyl cinnamate **4**. Leaching levels are also comparable; the percentage leaching represents the amount of palladium contamination with respect to the amount of palladium catalyst employed.⁸ TPPDS is readily accessible by this reported method and performs as well as TPPTS in biphasic palladium-catalysed Heck reactions.

Acknowledgements

We wish to thank AstraZeneca for the funding for this project.

References

- (a) Kuntz, E. G. *Chem. Tech.* **1987**, 520. (b) Herrmann, W. A.; Kohlpainter, C. W. *Angew. Chem., Int. Ed. Engl.* **1993**, 32, 1524–1544. (c) Cornils, B.; Kuntz, E. G. *J. Organomet. Chem.* **1995**, 502, 177–186.
- For a review on aqueous organometallic chemistry, see: Joó, F.; Kathó, A. *J. Mol. Catal.* **1997**, 116, 3–26.

3. Bartik, T.; Bartik, B.; Hanson, B. E.; Glass, T.; Bebout, W. *Inorg. Chem.* **1992**, *31*, 2667–2670. (b) Herrmann, W. A.; Albanese, G. P.; Manetsberger, R. B.; Lappe, P.; Bahrmann, H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 811–813. (c) Darensbourg, M. Y., Ed. *Inorganic Syntheses* **1998**, *32*, 14–16. (d) Hida, S.; Roman, P. J.; Bowden, A. A.; Atwood, J. D. *J. Coord. Chem.* **1998**, *43*, 345–348.
4. Triphenylphosphine was recrystallised from hot methanol before use.
5. Protonation of the phosphine provides stability against the oxidising nature of the oleum.
6. The addition of NaOH should take no less than 1 hour due to the exothermic nature of the reaction. It is at this stage that oxidation of the phosphorus is likely to occur. During the early stages of neutralisation the solution still has the potential to oxidise and oxidation is more likely at elevated temperatures.
7. Bhanage, B. M.; Zhao, F.-G.; Shirai, M.; Arai, M. *Tetrahedron Lett.* **1998**, *39*, 9509–9512. (b) Lemaire-Audoire, S.; Savignac, M.; Dupuis, C.; Genêt, J.-P. *Tetrahedron Lett.* **1996**, *37*, 2003–2006.
8. Leaching of palladium was determined as follows: The toluene phase was removed and all volatiles evaporated. The samples were then extracted with aqua regia (3:1 $\text{CHCl}_3:\text{HNO}_3$, 0.2 cm^3). Deionised water (5 cm^3) was then added and the samples centrifuged. Analysis was undertaken on a Perkin–Elmer 1100B atomic absorption instrument in conjunction with a series of Pd standards.