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Convenient synthesis of new amphiphilic triphenylphosphine analogues for aqueous biphasic catalysis

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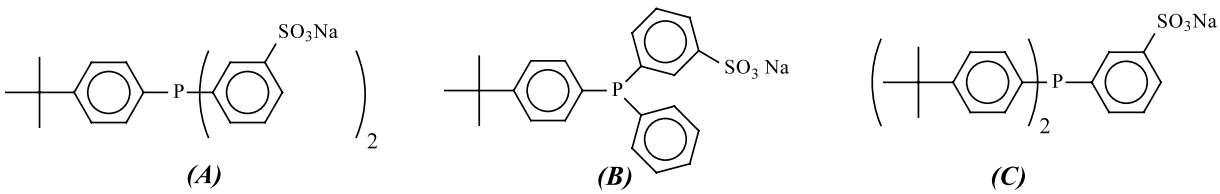
Abstract—The synthesis of three triphenylphosphine analogues with phenyl groups replaced by (4-*tert*-butyl)phenyl and (3-sulfonato)phenyl group is described. The surface-active properties of these new compounds are reported. The catalytic activities obtained with these phosphines in the palladium-catalyzed cleavage of undecyl allyl carbonate were up to 24000 times higher than those observed with trisulfonated triphenylphosphine, the ligand typically used in biphasic catalysis. One of these catalysts can be recovered six times without loss of catalytic activity. © 2001 Elsevier Science Ltd. All rights reserved.

The use of amphiphilic phosphines in aqueous organometallic catalysis is an attractive approach to increasing the reactivity of highly water insoluble substrates.[1] Indeed, amphiphilic phosphines which combine in the same molecule both functions of a ligand and a surfactant avoid addition of mass transfer promoters to the reaction medium. Although the synthesis of several amphiphilic phosphines has been described and their efficiency has been demonstrated in hydroformylation,[2] hydrogenation,[3] and carbon–carbon coupling reactions,[4] the use of amphiphilic phosphines in biphasic catalysis is not widespread and no industrial application has been developed so far. This may mainly result from the difficulty to prepare these compounds in a short and easy way. Indeed, the reported synthetic protocols usually require expensive or non-commercially available reagents, tedious work-up or long multistep reaction sequences.

We report herein an efficient and simple synthesis of amphiphilic phosphines and their behavior in biphasic catalysis. These new phosphines were prepared by reaction of the Grignard reagent $(CH_3)_3CC_6H_4MgBr$ with phosphorus (III) chloride reagents (e.g. $ClP(C_6H_5)_2$ or $Cl_2PC_6H_5$), followed by sulfonation of the corresponding phosphine. This two-step procedure affords three amphiphilic triphenylphosphine analogs **(*A*)**, **(*B*)** and **(*C*)** in moderate yields (45–65%). The 1-bromo-4-*tert*-butylbenzene is the key building block of this synthesis. Indeed, sulfonation of triarylphosphine bearing linear alkyl group (i.e. ethyl, heptyl or dodecyl chain) was unsuccessful due to the cleavage of the alkyl chain during the sulfonation process.

The surface activity of the phosphines was studied by surface tension measurements (Fig. 1). The trisulfonated triphenylphosphine (TPPTS), the ligand typi-



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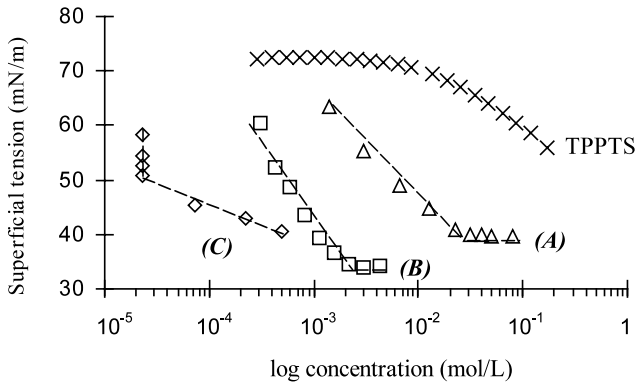


Figure 1. Surface tensions of aqueous solutions of TPPTS and phosphines **(*A*)**, **(*B*)**, **(*C*)** at 25°C.

cally used in biphasic catalysis, was also studied for comparison. The linear decrease in surface tension with log(c) until a minimum value indicates undoubtedly a surfactant behavior for phosphines **(*A*)**, **(*B*)** and **(*C*)**. In the case of TPPTS, the surface tension decreases much more slowly and does not reach a minimum value, thus confirming the hydrotropic behavior of TPPTS.[5] The critical micellar concentration for phosphines **(*A*)**, **(*B*)** and **(*C*)** was found to be 2.2×10^{-2}, 2×10^{-3} and 2.2×10^{-5} mol/L, respectively.

The efficiency of the amphiphilic triphenylphosphine analogues was investigated in a palladium-catalyzed cleavage reaction. As shown in Fig. 2, palladium(II) acetate associated with the phosphine **(*A*)**, **(*B*)** or **(*C*)** allows very rapid cleavage of undecyl allyl carbonate into undecanol. Indeed, whereas the conversion with the TPPTS ligand was only 3% after 24 h, 2 min, 45 min and 160 min are required for complete conversion with phosphines **(*C*)**, **(*B*)** and **(*A*)**, respectively. In terms of activity, the initial catalytic activities obtained with phosphine **(*A*)**, **(*B*)** and **(*C*)** were, respectively 300, 1100 and 24000 times higher than that observed with TPPTS. The product/catalyst separation efficiency was examined by performing a series of consecutive runs. The catalytic system based on phosphine **(*C*)** lost totally its original activity from the first run, indicating that the high activity observed with this ligand was due to the presence of catalyst in the organic phase. A slight decrease of ca 5% in the catalytic activity was observed between each run with the phosphine **(*B*)**, suggesting that this phosphine does not retain the palladium quantitatively in the aqueous phase. Interestingly, the catalyst generated from the phosphine **(*A*)** can be recovered at least six times without any loss in catalytic performances. Furthermore, the phase separation is easy and no formation of emulsions was observed. Obviously, this phosphine fulfills all requirements for catalysis in the aqueous phase.

In conclusion, synthesis of amphiphilic phosphines can be easily achieved in two steps by using a classic phosphine synthesis methodology from commercially available 1-bromo-4-*tert*-butylbenzene. This is due to the fact that the *tert*-butyl group is stable under the sulfonation conditions and avoids the sulfonation of the aromatic ring bearing it. Some fruitfull applications of phosphines **(*A*)** in aqueous organometallic catalysis should emerge in a next future.

1. General procedure for the synthesis of triarylphosphines

1.1. (4-*tert*-Butylphenyl)diphenylphosphine or bis-(4-*tert*-butylphenyl)phenylphosphine

These compounds were obtained on multigrams scale by a slightly modified published procedure.[6] To a suspension of magnesium (2.5 g, 103 mmol, 1.1 equiv.) in 50 mL of anhydrous THF was introduced under nitrogen 1-bromo-4-*tert*-butylbenzene (6.6 g, 31 mmol, 0.33 equiv.). After a few minutes, the reaction began and 13.2 g (62 mmol, 0.66 equiv.) of 1-bromo-4-*tert*-butylbenzene in THF (20 mL) was added dropwise. The

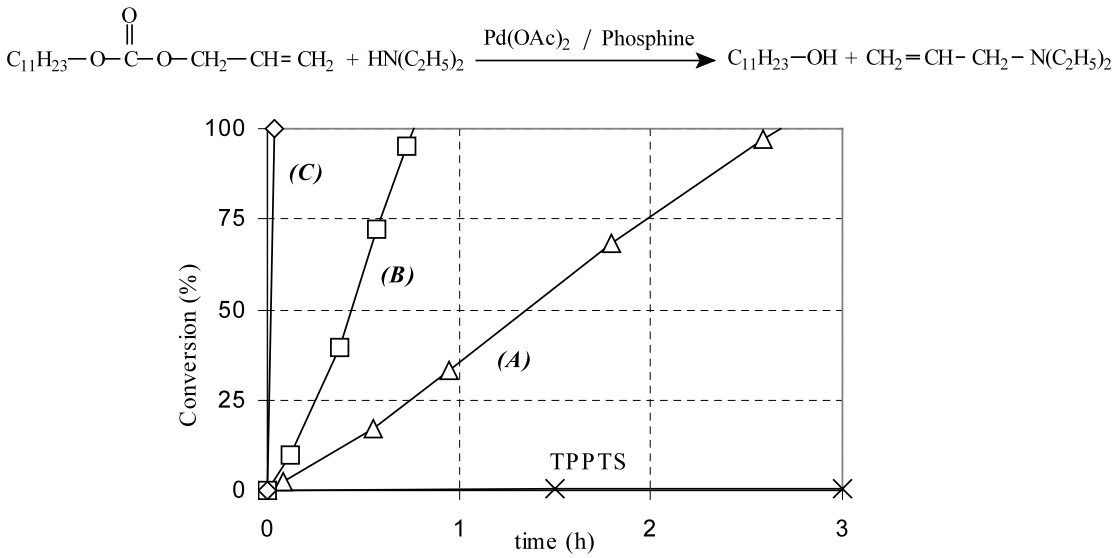


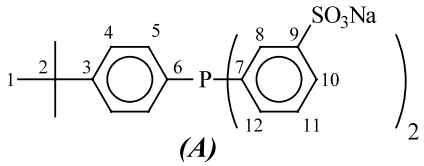
Figure 2. Catalytic cleavage of undecycl allyl carbonate in biphasic medium using TPPTS, phosphines **(*A*)**, **(*B*)** and **(*C*)** as ligand.

reaction mixture was then heated under reflux for 1 h. After cooling, chlorodiphenylphosphine (16.6 g, 75 mmol, 0.8 equiv.) or dichlorophenylphosphin (6.73 g, 38 mmol, 0.4 equiv.) in THF (10 mL) was added dropwise and then heated under reflux for 1 h. Once the reaction was complete, the mixture was poured into a mixture of ice (ca. 50 g) and HCl (100 mL, 1N) and stirred until magnesium dissolution. The aqueous phase was extracted with toluene (3×35 mL) and the combined organic layers were dried over anhydrous $MgSO_4$, filtered and concentrated by rotary evaporation. The resulting oil was recrystallized from methanol to give white crystals. Yield: ~90%.

2. General procedure for the synthesis of amphiphilic triphenylphosphine analogues

2.1. Bis-(3-sodium sulfonatophenyl)-(4-*tert*-butylphenyl)-phosphine (*A*)

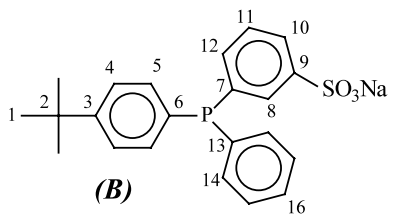
$P(Ph)_2(p\text{-}t\text{BuPh})$ (5 g, 15.7 mmol) was dissolved in concentrated sulfuric acid (18N, 96%, 8.5 mL). After cooling to 5°C, the oleum (65%, 10.6 mL) was added slowly under vigorous stirring and keeping the temperature under 10°C. The reaction mixture was then kept at room temperature for 40 h. Excess of oleum was neutralized by addition of 50 ml of degassed water. The mixture was poured into mixture of ice (250 g) and water (250 mL) and dipentyl amine (4.94 g, 31 mmol, 1 equiv. per sulfonate group) was then added. The ammonium salt of the sulfonated phosphine was recovered from the acidic aqueous layer by addition of ethyl acetate (3×60 mL). The organic phase was washed with water (20×100 mL), dried over anhydrous $MgSO_4$, filtered and concentrated by rotary evaporation. The resulting oil was dissolved into isoamylic alcohol and extracted eight times with a mixture of water (10 mL) and NaOH (2 mL, 2N). The first and second fraction containing mainly sulfate ions and phosphine oxide was kept away. The others were concentrated in vacuo and a white solid was obtained. This solid was recystallised from methanol to give white crystals. Yield: 5.32 g (65%); ^{1}H NMR: (D_2O) 1.14 (9H, s, H_1), 7.34 (2H, t, $^3J_{PH} \sim {}^3J_{HH} = 8.3$ Hz, H_5), 7.50 (2H, t, $^3J_{PH} \sim {}^3J_{HH} = 7$ Hz, H_{12}), 7.55 (4H, m, $H_{4,11}$), 7.77 (2H, d, $^3J_{PH} = 7.8$ Hz, H_8), 7.82 (2H, d, $^3J_{HH} = 7.8$ Hz, H_{10}); $^{13}C\{^1H\}$ NMR: (D_2O) 30.9 (C_1, s), 34.6 (C_2, s), 126.3 (C_{11}, d, $^3J_{PC} = 7$ Hz), 126.7 (C_{10}, s), 129.9 (C_4, d, $^3J_{PC} = 6$ Hz), 130.6 (C_8, d, $^2J_{PC} = 25$ Hz), 132.0 (C_6, d, $^1J_{PC} = 9$ Hz), 133.8 (C_{12}, d, $^2J_{PC} = 20$ Hz), 136.5 (C_5, d, $^2J_{PC} = 16$ Hz), 137.6 (C_7, d, $^1J_{PC} = 10$ Hz), 143.3 (C_9, d, $^3J_{PC} = 8$ Hz), 154.0 (C_3, s); $P\{^1H\}$ NMR: (D_2O, external H_3PO_4) −7.7 (s) FTIR (KBr) ν (cm^{-1}): 2964 (m), 2869 (w), 1461 (w), 1447 (w), 1390 (m), 1366 (w), 1306 (w), 1201 (s), 1080 (w), 848 (w), 831 (m), 826 (w), 785 (m), 680 (m), 518 (m). Anal. calcd for $C_{22}H_{21}Na_2O_6PS_2 \cdot 4H_2O$ ($M = 594$ g mol^{-1}): C, 44.44; H, 4.88. Found: C, 44.51; H, 4.67.



(A)

2.2. Phenyl-(3-sodium sulfonatophenyl)-(4-*tert*-butylphenyl)-phosphine (*B*)

$P(Ph)_2(p\text{-}t\text{BuPh})$ (5 g, 15.7 mmol) was dissolved in concentrated sulfuric acid (18N, 96%, 27 mL). After cooling to 5°C, the oleum (65%, 15 mL) was added slowly under vigorous stirring and keeping the temperature under 10°C. The reaction mixture was then kept at room temperature for 2 h. The neutralization was carried out under nitrogen atmosphere at 0°C by the slow, dropwise addition of NaOH (380 mL, 5.5N). The water was removed under vacuum. The remaining solid was refluxed in methanol (150 mL) for 30 min and the solution filtered hot to remove the sodium sulfate. The solution was then evaporated to give a white solid which was recrystallized from methanol to give white crystals. Yield: 3.96 g (60%); ^{1}H NMR: (D_2O) 0.9 (9H, s, H_1), 6.82 (11H, um, $H_{4,5,11,12,14,15,16}$), 7.51 (1H, d, $^3J_{HH} = 7$ Hz, H_{10}), 7.60 (1H, d, $^3J_{PH} = 8.1$ Hz, H_8); $^{13}C\{^1H\}$ NMR: (D_2O) 31.2 (C_1, s), 34.5 (C_2, s), 125.8 (C_4, d, $^3J_{PC} = 7$ Hz), 126.5 (C_{10}, s), 129.0 (C_{15}, d, $^3J_{PC} = 7$ Hz), 129.5 ($C_{11,16}$, br s), 130.7 (C_8, d, $^2J_{PC} = 27$ Hz), 133.1 (C_6, d, $^1J_{PC} = 10$ Hz), 133.9 ($C_{14,5}$, t, $^2J_{PC} = 19$ Hz), 135.4 (C_{12}, d, $^2J_{PC} = 11$ Hz), 136.2 (C_{13}, d, $^1J_{PC} = 10$ Hz), 138.4 (C_7, d, $^1J_{PC} = 13$ Hz), 143.8 (C_9, d, $^3J_{PC} = 7$ Hz), 151.7 (C_3, s); $^{31}P\{^1H\}$ NMR: (D_2O, external H_3PO_4) −7.1 (s) IRFT (KBr) ν (cm^{-1}): 2962 (vs), 2867 (m), 1457 (m), 1434 (m), 1389 (m), 1362 (m), 1340 (m), 1310 (m), 1215 (s), 1082 (s), 841 (m), 827 (m), 788 (w), 746 (m), 675 (m), 582 (m), 560 (m), 501 (m). Anal. calcd for $C_{22}H_{22}NaO_3PS \cdot 2H_2O$ ($M = 456$ g mol^{-1}): C, 57.33; H, 5.7. Found: C, 57.54; H, 5.29.

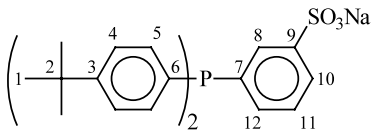


(B)

2.3. Bis-(4-*tert*-butylphenyl)-(3-sodium sulfonatophenyl)phosphine (*C*)

$PPh(p\text{-}t\text{BuPh})_2$ (5 g, 13.37 mmol) was dissolved in concentrated sulfuric acid (18N, 96%, 12 mL). After cooling to 5°C, the oleum (65%, 8 mL) was added slowly under vigorous stirring and keeping the temperature under 10°C. The reaction mixture was then kept at room temperature for 18 h. Excess of oleum was neutralized by addition of 50 ml of degassed water. The mixture was poured into mixture of ice (100 g) and water (100 mL) and dipentyl amine (2.1 g, 13.37 mmol, 1 equiv. per sulfonate group) was then added. The ammonium salt of the sulfonated phosphine was recovered from the acidic aqueous layer by addition of ethyl acetate (3×75 mL). The combined organic phases were washed with water (20×100 mL), dried over anhydrous $MgSO_4$, filtered and concentrated by rotary evaporation. Dissolution of the resulting oil in isoamylic alcohol (70 mL) followed by the dropwise addition of NaOH (90 mL, 0.15N) caused the precipitation of a white solid. This solid was filtered, triturated and washed with warm heptane to give a white solid. Yield: 3.18 g (50%); ^{1}H NMR: (DMSO) 1.27 (18 H, s, H_1), 7.15 (1H, t, $^3J_{HH} \sim {}^3J_{HP} = 7$ Hz, H_{12}), 7.21 (4H,

t, $^3J_{HH} \sim {}^3J_{HP} = 8$ Hz, H_5), 7.35 (1H, t, $^3J_{HH} = 8$ Hz, H_{11}), 7.44 (4H, d, $^3J_{HH} = 8$ Hz, H_4), 7.59 (2H, d, $J = 7$ Hz, $H_{8,10}$); $^{13}C\{^1H\}$ NMR: (DMSO) 32.02 (C_1, s), 35.5 (C_2, s), 126.5 (C_4, d, $^3J_{PC} = 8$ Hz), 126.9 (C_{10}, s), 129.0 (C_{11}, d, $^3J_{PC} = 6$ Hz), 130.8 (C_8, d, $^2J_{PC} = 21$ Hz), 133.9 (C_{12}, d, $^2J_{PC} = 19$ Hz), 134.3 (C_6, d, $^1J_{PC} = 10$ Hz), 134.9 (C_5, d, $^2J_{PC} = 20$ Hz), 137.7 (C_7, d, $^1J_{PC} = 13$ Hz), 149.4 (C_9, d, $^3J_{PC} = 6$ Hz), 152.4 (C_3, s); $P\{^1H\}$ NMR: (DMSO, external H_3PO_4) −7.6 (s) FTIR (KBr) ν (cm^{-1}): 2961 (s), 2866 (m), 1463 (m), 1392 (m), 1362 (m), 1310 (w), 1201 (s), 1081 (m), 841 (w), 827 (s), 823 (s), 788 (m), 746 (w), 677 (s), 518 (w). Anal. calcd for $C_{26}H_{30}NaO_3PS{\cdot}2H_2O$ ($M = 512$ g mol^{-1}): C, 60.94; H, 6.64. Found: C, 60.54; H, 6.59.



(C)

3. General procedure for the catalytic and recycling experiments

3.1. Catalytic experiments

$Pd(OAc)_2$ (0.134 mmol, 30 mg), phosphine (1.20 mmol) and water (6 g) were introduced under nitrogen atmosphere into a Schlenk tube. After stirring with a magnetic bar for 1 h, the yellow solution was transferred into a mixture of undecyl allyl carbonate (3.35 mmol), diethylamine (6.67 mmol, 0.49 g) and heptane (6 g). The medium was stirred at 1000 rpm at room temperature and the reaction was monitored by quantitative gas chromatographic analysis of the organic layer.

3.2. Recycling experiments

The first batch was carried out as described above. When the reaction was complete, the aqueous and organic phases were separated. The aqueous phase was left in the bottom of the reactor and a new carefully deoxygenated solution of heptane/allyl undecyl carbonate/diethylamine was introduced. All steps were performed under a nitrogen atmosphere.

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