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Synthesis of air-stable zwitterionic 2-phosphiniminium-arenesulfonates

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ABSTRACT

Efficient synthetic methodology for preparation of 2-phosphiniminium-5-methylbenzenesulfonate zwitterions is reported. Staudinger reaction between phosphines and *n*-propyl 2-azido-5-methylbenzenesulfonates followed by sulfonate ester deprotection using pyridinium tetrafluoroborate/pyridine afforded the zwitterions in excellent yields. This new route directly accesses *ortho*-substituted-arenesulfonate ligands that incorporate a phosphinimine, a strong σ-donor.

Introduction

We have recently begun a program on the synthesis, study, and application of *ortho*-phosphinimine-arenesulfonates (NPSO) in organometallic and organic catalysis.[1] Anionic phosphinimide donors have been exploited extensively as ancillary ligands for both early and late transition metals.[2] Less extensively explored, the coordination chemistry of neutral phosphinimines, both as monodentate and bidentate ligands, is beginning to receive attention.[3] These ligands act as good electron-donor ligands toward transition metals and are able to form strong metal–nitrogen bonds. This ability is due to the fact that delocalization about the phosphinimine PN moiety produces compounds with enhanced basicity and nucleophilicity.[4] The excellent donor properties of neutral phosphinimine ligands were elucidated by the synthesis of tungsten tetracarbonyl complexes containing benzene bridged bidentate phosphinimine-imine ligands.[3e] The ν_{CO} values for these tungsten complexes are some of the lowest values reported for bidentate bis-nitrogen ligands on tetracarbonyltungsten(0) groups. The low ν_{CO} values indicate that a phosphinimine is a strong σ-donor and a poor π-acceptor ligand versus comparable tetracarbonyltungsten(0) complexes that contain benzene bridged bidentate iminophosphine ligands.[5]

As well as being strong σ-donor ligands, when neutral phosphinimines with the P atom exocyclic to the chelate ring coordinate to transition metals via nitrogen the steric bulk is slightly removed from the metal center.[3b] This confers a second coordination sphere environment that contains steric bulk to protect a metal while leaving the first coordination sphere more open.[2a] To date, few examples exist where an exocyclic phosphinimine group has been incorporated into a mixed donor ligand system for use in the synthesis of late transition metal complexes.[3c–e] We present here an efficient and modular synthesis for preparing 2-phosphiniminium-5-methylbenzenesulfonate zwitterions.

Results and discussion

There are relatively few examples of *ortho*-substituted arenesulfonate bidentate ligands described. The first are the 2-phosphine-arenesulfonate ligands (PSO, **A**, Fig. 1) which have received considerable attention in the last decade as ancillary ligands for Pd(II) and Ni(II) olefin insertion polymerization catalysts.[6] PSO ligands have also been used to stabilize ruthenium complexes that catalyze allylic alkylations of heterocycles and amines.[7] The second, chiral *ortho*-NHC-benzenesulfonate ligands (**B**, Fig. 1), were reported by Hoveyda and have been used in the copper-catalyzed asymmetric conjugate addition, allylic alkylation, hydroboration, and diboronation reactions.[8]

Based on the literature, we realized that the best route to our NPSO ligands was to use commercially available 2-aminobenzenesulfonic acids. Protection of the sulfonic acid group as an alkyl ester allowed for the clean conversion of the 2-amino group to a phosphinimine. Phosphinimines, while relatively air stable, decompose under the relatively harsh deprotection conditions (acetic acid at 110 °C) used by Hoveyda in the synthesis of **B** to form $Ph_3P{=}O$ and an aryl amine. Other deprotection routes were explored.[9]

The NPSO alkyl esters **4–9** were synthesized in good yields by a 4 step reaction sequence. Protected 2-amino-5-methylbenzenesulfonate esters can be prepared on a multi gram scale in two steps as shown in Scheme 1. We successfully converted 2-amino-5-methyl-

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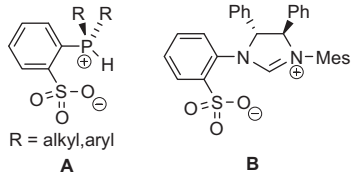


Figure 1. *ortho*-Substituted benzenesulfonate bidentate zwitterions.

benzenesulfonic acid into 2-amino-5-methylbenzenesulfonyl chloride (**1**) in 80% yield.[10] The 2-amino-5-methylbenzenesulfonyl chloride was converted into one of the four alkyl-2-amino-5-methylbenzene sulfonate esters (**2a–c**) in 81–93% yield by the reaction of **1** with the corresponding alcohol in the presence of 1,4-diazabicyclo[2.2.2]octane (DABCO).[9,11]

The amino esters **2a–c** were converted into their corresponding alkyl 2-azido-5-methylbenzenesulfonate esters (**3a–c**) via diazotization of the amine followed by reaction with sodium azide in water (Scheme 1). Azides **3a** and **3b** were isolated as solids while **3c** was isolated as an oil, all in good yields (71–83%). The 2-phosphinimine-5-methyl-benzenesulfonate esters (**4–9**) were synthesized by employing the Staudinger reaction between azides **3a–c** and PPh_3, Ph_2PMe, $(m\text{-tolyl})_3P$, and $(p\text{-tolyl})_3P$ (Scheme 1).[12] When phosphines were added to toluene solutions of azides **3a–c** rapid nitrogen evolution was observed at 25 °C and all reactions were complete in 4 h at 25 °C.[13] Compounds **4–9** were characterized by ^1H, ^{13}C, and ^{31}P NMR. The ^{31}P NMR chemical shifts for the isolated phosphinimines fall in the range of 3.2–2.2 ppm which is consistent with the values for aryl phosphinimines observed in the literature (δ = 10–0 ppm).[14] Phosphinimine formation was not observed between $(o\text{-tolyl})_3P$ and azide **3b** even when the reaction was heated at 60 °C in toluene for 12 h.[15] We believe the lack of reactivity between **3b** and $(o\text{-tolyl})_3P$ can be explained by comparing the steric bulk of $(o\text{-tolyl})_3P$ and PPh_3 using cone angles.[16] The smaller PPh_3 (Θ = 145°) can approach and react with azide **3b** to form a phosphazide intermediate which decomposes via loss of N_2 to form **5** even in the presence of the bulky *ortho*-alkyl sulfonate ester. Steric repulsion between the much bulkier $(o\text{-tolyl})_3P$ (Θ = 194°) and the *ortho*-alkyl sulfonate ester in **3b** prevents the formation of a phosphazide and thus the phosphinimine cannot form.[17]

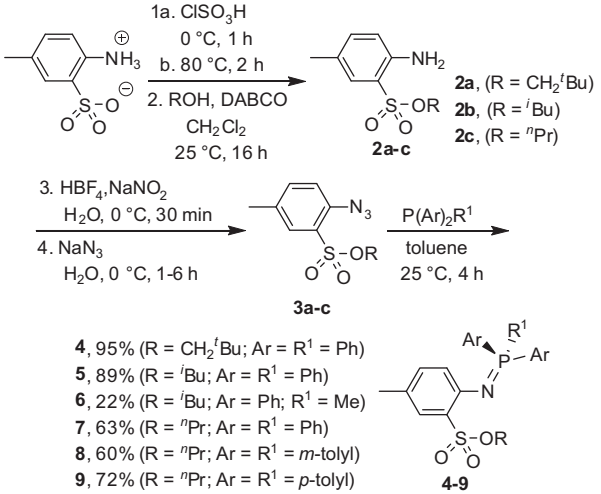
Synthesis of discrete metal complexes using our NPSO ligands requires deprotection of 2-phosphinimine-arenesulfonate esters **4–9**. A common deprotection route is the S_N2 reaction between iodide and an alkyl sulfonate ester in acetone.[18] Acetone is not acceptable as a solvent in these reactions due to the potential Aza-Wittig reaction between phosphinimines **4–9** and acetone forming the corresponding dimethylimine and $Ph_3P{=}O$.[12] In contrast to a literature report describing quantitative deprotection of pentyl benzenesulfonate by $[^nBu_4N][I]$ in refluxing C_6H_6 in 10 min,[19a] we found no reaction occurred when isobutyl ester **5** was refluxed for 12 h with 2 equiv of $[^nBu_4N][I]$ in C_6H_6.[19b]

Widlanski reported that isobutyl benzenesulfate was deprotected by piperidine (1 equiv) in $CDCl_3$ at 25 °C in 100% yield after 24 h.[20] No deprotection of isobutyl ester **5** was observed in $CDCl_3$ using piperidine (1 or 3 equiv) even when the reaction was refluxed for 24 h. We believe the lack of reactivity is due to the presence of the bulky phosphinimine group *ortho* to the sulfonate ester which prevents proper approach of piperidine to allow for displacement of the isobutyl group. Ester **7** was reacted with piperidine (5 equiv) in $CDCl_3$ at 68 °C. After 96 h heating, we observed 80% conversion of **7** to *N*-propyl-piperidinium 2-triphenylphosphinimine-5-methylbenezenesulfonate (**10**) with only 3% $Ph_3P{=}O$ present.[21] While the deprotection of **7** with piperidine to form **10** was successful the reaction rate was less than ideal. Based on our success using piperidine for the deprotection of **7**, we turned our attention to protonation of **7** prior to deprotection by a nucleophilic nitrogen base.

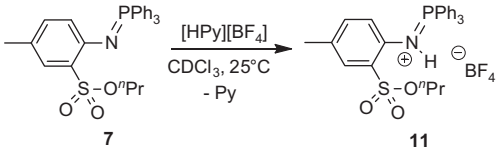
We envisioned phosphinimine protonation and propyl sulfonate ester deprotection by the liberated base could be carried out in a single reaction vessel. In choosing an appropriate H^+ source to protonate the phosphinimine nitrogen of **7** we wanted an acid whose conjugate base could not deprotonate the resulting phosphiniminium salt.[22] We chose to use pyridinium tetrafluoroborate as our H^+ source (pK_a = 5.2) and felt the free pyridine may be competent for the deprotection reaction.[22b] Indeed, rapid and complete protonation of **7** is achieved by using [HPy][BF_4] at 25 °C in $CDCl_3$ (Scheme 2).

The phosphiniminium N–*H* of **11** was not observed in the ^1H spectrum, but the ^{31}P NMR spectrum confirmed **11** (δ = 25 ppm).[14] When this sample was allowed to sit for 24 h at 25 °C, 30% of **11** had reacted with the pyridine to form 2-triphenylphosphiniminium-5-methylbenzene- sulfonate (**12**) and *N*-propylpyridinium tetrafluoroborate. We have found that the deprotection reaction of **11** with pyridine to form **12** proceeds at a faster rate when it is heated.[23] Combining [HPy][BF_4] with **7–9** in CH_2Cl_2 in the presence of excess pyridine and then refluxing the solution overnight forms NPSO zwitterions **12–14** in good yields (Scheme 3). Zwitterions **12–14** are air stable and can be isolated using column chromatography.[24]

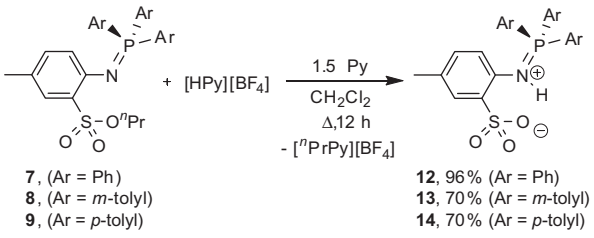
To confirm the structure of **12**, a crystal suitable for X-ray crystallography was obtained by slow diffusion of benzene into a CH_2Cl_2 solution of **12** at 23 °C. An ORTEP diagram of the corresponding structure is shown in Figure 2 with selected bond distances and angles listed. The structure of **12** shows the presence of the phosphiniminium group in which N(1) is protonated. The P(1)–N(1) bond distance [1.6327(17) Å] suggests a high degree of single bond character much like the P–N single bond found in $[Ph_3PN(H)Ph][Cl_2Pd(C_8H_{11})]$ [1.624(3) Å] and $[Ph_3PN(H)Ph][BF_4]$



Scheme 1. Synthesis of 2-phosphinimine-5-methyl-benzenesulfonate esters.



Scheme 2. Protonation of NPSO ester **7**.



Scheme 3. Synthesis of NPSO zwitterions **12**–**14**.

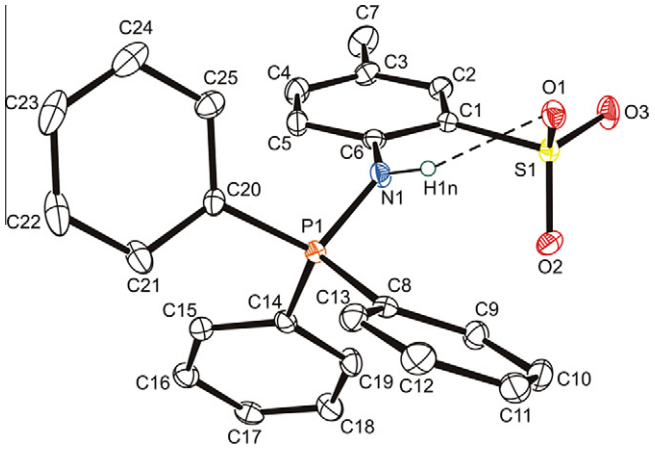
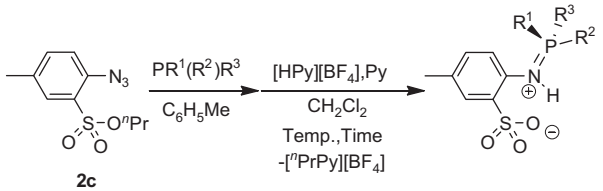


Figure 2. *ORTEP*-3[26] diagram of **12** showing 50% ellipsoids. H atoms are omitted for clarity with the exception of H1n which shows a strong intramolecular interaction: N1–H1n, 0.79(2) Å; O1—H1n, 2.07(3) Å; N1–H1n—O1, 143.6(3)°. Selected bond lengths (Å) P1-N1, 1.6327(17); N1-C6, 1.422(3); S1–C1, 1.784(2).

[1.635(4) Å] as well as the P–N single bond in the endocyclic phosphiniminium group of [4-(2,6-^{i}Pr$_2$C$_6$H$_3$)N(H)PPh$_2$)C$_{12}$H$_7$O][SO$_3$CF$_3$] [1.633(2) Å].[25a,25b,3h] The P(1)–N(1) bond distance in **12** is significantly longer than that found in the free phosphinimines Ph$_3$P=NPh [1.603(3) Å] and 4-(2,6-^{i}Pr$_2$C$_6$H$_3$)NPPh$_2$)C$_{12}$H$_7$O [1.559(2) Å].[25c,3h] In addition, the triphenylphosphine group on the nitrogen atom of the phosphiniminium is situated below the arene ring plane of the 5-methylbenzenesulfonate fragment with a C5–C6–N1–P1 torsion angle of 39.2(3)°.

With zwitterions **12**–**14** in hand, we envisioned the possibility to overcome the low yields of the NPSO sulfonate esters and to shorten the synthesis. We combined the Staudinger reaction with the [HPy][BF$_4$]/pyridine deprotection sequence in a single reaction flask, thus avoiding isolation of the NPSO sulfonate esters altogether. We reacted azide **2c** with Ph$_2$PMe in toluene at 25 °C for 2 h, removed the toluene under vacuum, and dissolved the residue in CH$_2$Cl$_2$. [HPy][BF$_4$] and excess pyridine were added to the CH$_2$Cl$_2$



12, 70%, reflux/12 h (R^1,R^2,R^3 = Ph)
15, 70%, reflux/12 h (R^1 = Me; R^2,R^3 = Ph)
16, 70%, 25 °C/48 h (R^1,R^2 = Me ;R^3 = Ph)
17, 65%, reflux/12 h (R^1 = Bn ;R^2,R^3 = Ph)
18, 70%, 25 °C/72 h (R^1,R^2,R^3 = Bn)

Scheme 4. 'One Pot' synthesis of 2-phosphiniminium-arene-sulfonate zwitterions.

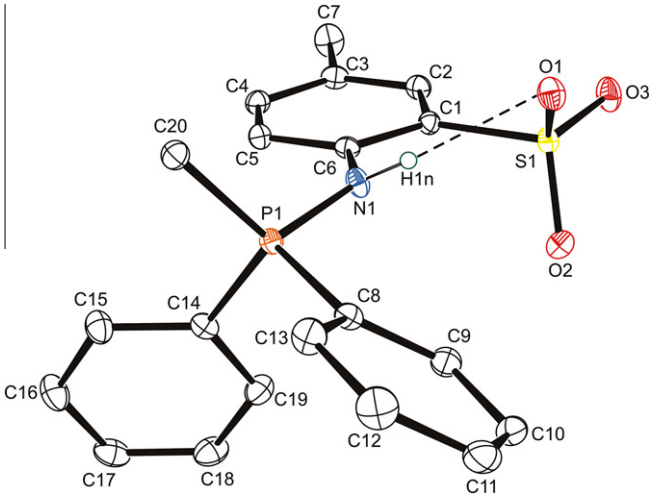


Figure 3. *ORTEP*-3[26] diagram of **15** showing 50% ellipsoids. H atoms are omitted for clarity with the exception of H1n which shows a strong intramolecular interaction: N1–H1n, 0.81(2) Å; O1—H1n, 2.12(3) Å; N1–H1n—O1, 140.7(3)°. Selected bond lengths (Å): P1–N1, 1.6380(12); N1–C6, 1.4124(17); S1–C1, 1.7811(14).

solution which was refluxed overnight. Gratifyingly, after work-up the Ph$_2$PMe NPSO zwitterion **15** was isolated in 70% yield (Scheme 4). This is a marked improvement on the low yield obtained for NPSO sulfonate ester **6**. We have applied our "one pot" synthesis to multiple commercially available phosphines and isolated zwitterions **12** and **15**–**18** in good yields. In the case of the more electron rich phosphines, PhPMe$_2$ (**16**) and Bn$_3$P (**18**), we found that optimal yields were obtained by stirring the [HPy][BF$_4$]/pyridine CH$_2$Cl$_2$ solution at 25 °C for 48 and 72 h respectively instead of refluxing for 12 h. The ^{31}P NMR chemical shifts for **12** and **15**–**18** are consistent with values for phosphiniminium salts observed in the literature.[3h,14,27]

The X-ray crystal structure of **15** is shown in Figure 3. Suitable crystals were obtained by slow diffusion of pentane into a CH$_3$OH solution of **15** at 23 °C. Similar to the structure of **12**, a phosphiniminium N–H is also present in **15**. The P(1)–N(1) bond distance [1.6380(12) Å] is statistically the same as the phosphiniminium P–N bond in **12** again supporting single bond character.[25] The phosphiniminium Ph$_2$PMe substituent in **15** has much less steric effect than the Ph$_3$P of **12**. Again the phosphorous atom of the phosphiniminium is situated below the plane of the aryl ring of the 5-methylbenzenesulfonate fragment but the C5–C6–N1–P1 torsion angle in **15** is greatly reduced 14.9(2)°.

In summary, we have developed a reliable synthetic protocol for preparing 2-phosphiniminium-5-methylbenzenesulfonates **12**–**18**. Their structures were unambiguously proven by multinuclear NMR and X-ray crystallography. This method represents an optimized, flexible synthetic route for directly accessing *ortho*-substituted-arenesulfonate ligands that incorporate phosphinimine functionality. The modular nature of this synthesis allows for the creation of a diverse ligand library where steric and electronic properties of the phosphinimine can be manipulated with ease. On-going studies in our laboratory are directed at developing catalytic organometallic late transition metal complexes derived from 2-phosphinimine-5-methylbenzenesulfonate ligands.

Acknowledgments

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Advanced Technology Research Center of the US Army, the Department of Energy (DEFG02-08CH11538), and the Kentucky Research Challenge Trust Fund for the upgrades of our X-ray facilities.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2012.06.112.

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13. Synthesis of NPSO ester **5** was attempted using amino ester **2b** and Ph_3PBr_2 in the presence of excess NEt_3. After work-up, **2b** was recovered along with $Ph_3P{=}O$ as the only phosphorous containing product.
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21. When using 10 or 20 equiv of piperidine, the rate of deprotection increased but the amount of Ph_3PO increased as well. For 10 equiv of piperidine, 83% of **10** was observed after 72 h with 9% Ph_3PO. For 20 equiv of piperidine, 88% of **10** was observed with 12% Ph_3PO present after 72 h.
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23. After 24 h at 68 °C, 85% conversion to **12** was observed. The protonated phosphonium group in **12** appears as a singlet at 31 ppm in the ^{31}P NMR while the N-*H* is visible in ^1H NMR spectrum as a sharp doublet at 10.22 ppm ($^2J_{P-H}$ = 10 Hz). No Ph_3PO is observed in any of the reactions of **9** with [Hpy][BF_4] or **11** with pyridine.
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27. ^{31}P NMR shifts for zwitterions **12** and **15**–**18**; **12** (δ = 31.6 ppm), **13** (δ = 31.6 ppm), **14** (δ = 31.4 ppm), **15** (δ = 39.0 ppm), **16** (δ = 43.7 ppm), **17** (δ = 36.1 ppm), **18** (δ = 48.9 ppm). The N–*H* is visible in the downfield region of the ^1H NMR spectra of **12**–**18** as a sharp doublet ($^2J_{P-H}$ = 7–10 Hz) except for **15** whose ^1H NMR spectrum was recorded in CD_3OD due to poor solubility of **15** in CD_2Cl_2 or $CDCl_3$.