# Water-Soluble Derivatives of Furylphosphanes

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*Dedicated to Prof. Dr. Othmar Stelzer on the occasion of his 60th birthday.*

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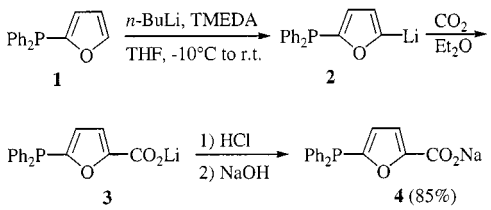
(2-Furyl)diphenylphosphane **(1)**, bis(2-furyl)phenylphosphane **(8)** and tris(2-furyl)phosphane **(9)** have been converted into their water soluble 5-carboxylates **4, 11** and **12**, 5-phosphonates **14** and **16** and 5-sulfinates **17**–**19**. In most cases, the selected route involved a 5-bromo to 5-lithio exchange reaction, followed by reaction with $CO_2$, $ClP(O)(OEt)_2$ or $SO_2$. The furan group sharply enhances the water-solubility of these products when compared with the corresponding benzene derivatives. Catalytic tests in hydrogenation, hydroformylation and Heck cross-coupling reactions showed that the sulfinate group tends to inhibit the catalysis and, in addition, a sharp drop in activity was observed with the trifunctional products **12** and **19**. Overall, the phosphonates **14** and **16** appear to be the most promising ligands for biphasic catalysis.

## Introduction

Recently, a great interest in furylphosphanes, especially tris(2-furyl)phosphane, has been evident in the literature because of their increasing use in homogeneous catalysis.[1] In many cases, for example in the Stille cross-coupling reaction, they have been shown to be significantly more efficient than their phenyl counterparts. In view of the tremendous development of aqueous two-phase catalysis,[2] the synthesis of water-soluble versions of these furylphosphanes is clearly a useful target. Since the replacement of a phenyl group by a furyl moiety is known to increase water solubility,[3] this was regarded as an additional incentive. We now describe our synthetic work in this area.

## Results and Discussion

Our initial synthetic strategy for water-soluble furylphosphanes was based on the metallation of the furan ring of 2-furylphosphanes by a lithiated base, followed by reaction of the resulting carbanion with an electrophile. Since the carboxylate group is one of the most frequently used water-solubilizing functionalities,[4] our first attempts were directed toward the synthesis of furylphosphanes 5-carboxylates as depicted in Scheme 1. The base of choice for the metallation of furyldiphenylphosphanes **1** ($n$ = 1) was found to be $n$BuLi/TMEDA in THF at between −10 °C and room temperature. The resulting 2-phosphinylated 5-lithiofuryl carbanion **2**, which was observed cleanly and quantitatively by $^{31}P$ NMR spectroscopy, was then reacted at low temperature with a saturated ethereal solution of dry ice (Scheme 1).




Scheme 1. Synthesis of 5-carboxylate diphenylfurylphosphane

The crude lithiated product **3** was isolated as a hygroscopic white powder which was purified by repeated washing with $Et_2O$ and then converted into its sodium salt **4** in 85% overall yield.

The synthesis of the di- **11** and tricarboxylates **12** derived from phenyldifuryl- **8** and trifurylphosphanes **9** proved more difficult. Indeed, clean, complete dilithiation and trilithiation of the corresponding phenyldifuryl- **8** and trifurylphosphanes **9** using $n$BuLi, TMEDA was impossible. Consequently, reaction with an ethereal solution of dry ice gave an isolated product mixture containing mono-, di- and tricarboxylate derivatives and valeric acid derived from carbonation of unchanged $n$BuLi. Hence, it was necessary to devise a method for the quantitative metallation of 2-furylphosphanes **8** and **9** in their 5-positions without the need for excess metallating agent. Thus the initial synthetic procedure was altered to replace the proton-metal exchange in the α-furanic position by an halogen-metal exchange reaction.

Two approaches to 5-bromofurylphosphanes were developed (Schemes 2 and 3). Furan was first metallated as described in Scheme 1, then reacted at −40 °C with dibromotetrafluoroethane, whose use as a brominating agent is

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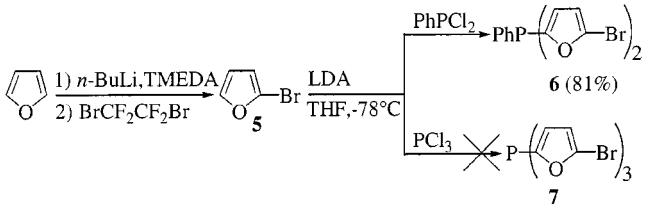
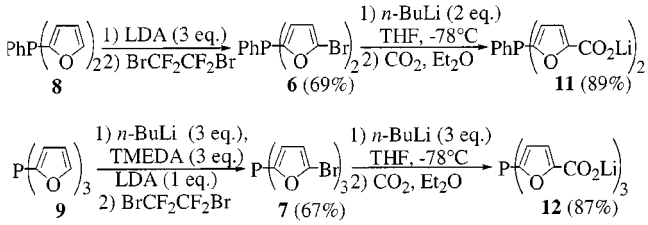
well documented.[5] Bromofuran **5**, which was formed quantitatively, was in turn metallated in 5-position with LDA at room temperature in the same vessel, then treated at low temperature with the chlorophosphanes. Under these conditions, the bis[2-(5-bromofuryl)]phenylphosphane **6** was produced cleanly in 81% isolated yield. Unfortunately, the 5-lithiofuryl carbanion derived from **5** did not react satisfactorily with $PCl_3$ and tris[2-(5-bromofuryl)]phosphane **7** was never observed by $^{31}P$ NMR spectroscopy (Scheme 2).




Scheme 2. Synthesis of the bis[2-(5-bromofuryl)]phenylphosphane

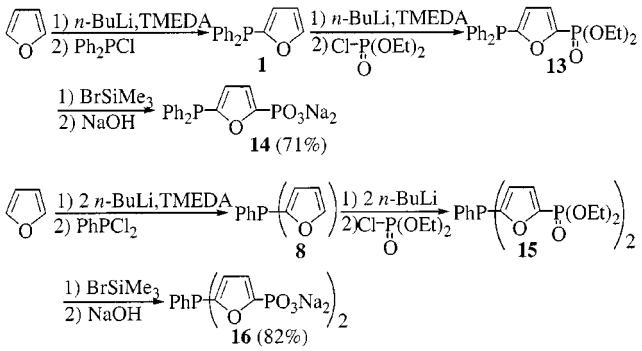
The lack of generality in the previous approach led us to reverse the order of functionalization and to effect the phosphinylation of the furan ring prior to the introduction of the bromine atom (Scheme 3). Thus, the phenyldifuryl- **8** and trifurylphosphanes **9** were metallated with *n*BuLi in the presence of LDA at between −40 and −20 °C in THF. For complete metallation, excess base (3 equiv. for **8** and 4 equiv. for **9**) was needed to generate the corresponding 5-lithiofuryl carbanions. These were reacted with $BrCF_2CF_2Br$ at −60 °C to produce the crystalline bis[2-(5-bromofuryl)]phenylphosphane **(6)** and tris[2-(5-bromofuryl)] phosphane **(7)** in 67−69% yields. This methodology has been extended to the synthesis of tris[2-(5-chlorofuryl)]-phosphane **(10)** in 77% yield under the same experimental conditions with hexachloroethane as the chlorinating agent.




Scheme 3. Bromation of phenyldifuryl- and trifurylphosphanes

This straightforward access to the 2-(5-bromofuryl)phosphanes **6** and **7** provides a convenient route to the corresponding carboxylates. The bromine-lithium exchange reaction with *n*BuLi is complete at low temperature and cleanly produced the corresponding 5-lithiofuryl carbanions which were then reacted with an saturated ethereal solution of dry ice. The synthesis of the di- **11** and tricarboxylates **12** is summarized in Scheme 3. The reactions were essentially quantitative and the lithiated carboxylates **11** and **12** were recovered by precipitation in $Et_2O$.

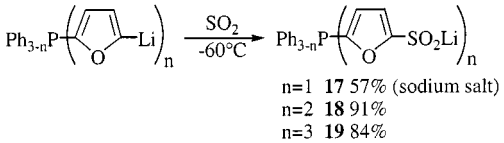
The phosphonate group is another solubilizing functionality which has recently been introduced.[6] We have been able to prepare mono- **13** and diphosphonates **15** in a one-pot procedure from diphenylfuryl- and phenyldifuryl-phosphanes (Scheme 4). In a typical procedure, furan was metallated as described in Scheme 1 then reacted with the corresponding chlorodiphenyl- and dichlorophenylphosphanes at −60 °C to give the phosphanes **1** and **8**. Subsequently, formation of the 5-lithiofuryl derivatives was effected by metallation with *n*BuLi and the resulting carbanion was then added to diethylchlorophosphate at −78 °C. After workup and purification by chromatography, the phosphorylated furylphosphanes **13** and **15** were isolated in 70 and 40% yields, respectively. The diethoxyphosphoryl group grafted on the furan ring was then converted into its silyl diester,[7] hydrolyzed, and finally converted into the sodium salt with a stoichiometric quantity of NaOH (Scheme 4).




Scheme 4. Synthesis of the 5-phosphonates 2-furyl- and 2-difurylphosphanes

All our attempts to prepare pure samples of the corresponding tris-phosphonate by methods analogous to those employed for the tris-carboxylate **12** gave unsatisfactory results, even when starting from tris[2-(5-bromofuryl)]phosphane **(7)**.

We are unaware of any literature reference to the use of the sulfinate group as a water-solubilizing functionality. The furylsulfinates are easily prepared by reaction of $SO_2$ with the organolithium derivatives of furans.[8] Thus the mono- **17**, di- **18** and tri-sulfinates **19** were readily obtained *via* a straightforward transposition of the syntheses of mono- di- and tricarboxylates by simple replacement of $CO_2$ with $SO_2$ (Scheme 5).




Scheme 5. Synthesis of the 5-sulfinates 2-furyl-, 2-difuryl- and 2-trifurylphosphanes

The yields of the sulfinates were practically quantitative. Since both $SO_2$ and $RSO_2H$ are known to oxidize tertiary phosphanes,[9] careful elimination of excess $SO_2$ by bubbling $N_2$ through the crude reaction mixture is necessary prior to isolation. The sulfinic acids are intrinsically unstable, but their lithium salts can be kept without oxidation up to *ca* 80 °C. Obviously, the negative charge prevents any nucleophilic attack of the phosphorus lone pair at sulfur.

Table 1. Water-solubility of functional furylphosphanes

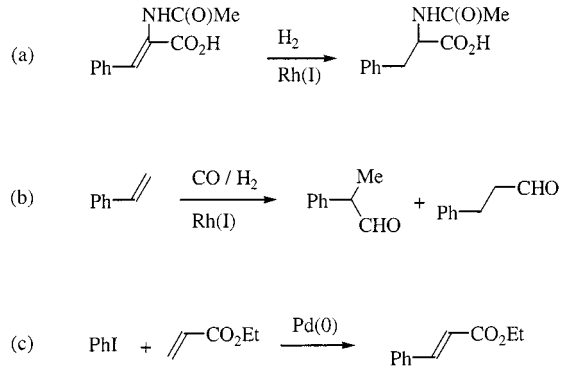
| Compound | Temperature [°C] | Solubility [g·L$^{-1}$] | Solubility [mol·L$^{-1}$] |
|---|---|---|---|
| **4** ($Na^+$) | 23 | 250 | 0.8 |
| **11** ($Li^+$) | 23 | 620 | 1.8 |
| **12** ($Li^+$) | 23 | 950 | 2.5 |
| **14** ($Na^+$) | 20 | 680 | 1.8 |
| **16** ($Na^+$) | 23 | 1140 | 2.3 |
| **17** ($Na^+$) | 21 | 205 | 0.6 |
| **18** ($Li^+$) | 21 | 660 | 1.7 |
| **19** ($Li^+$) | 23 | 1150 | 2.6 |

All attempts to introduce the ubiquitous sulfonate hydrosolubilizing group were unsuccessful. These included the synthesis of sulfonates *via* the reaction of the organolithium **2**, with $SO_3$ tertiary amine adducts[10] which gave starting materials, or with $ClSO_3SiMe_3$ which gave the 5-($SiMe_3$) derivative, and with $ClSnBu_3$. This last reaction was investigated by analogy with a published synthesis of furylsulfonates[11] using $ClSO_3SiMe_3$. Only a sulfonylated phosphane oxide was obtained. Its formula was unequivocally established on the basis of the following data: the $^{31}P$ resonance of the oxide in water appears at $\delta = +21.4$ *versus* $\delta = -25$ for **1**. The $^1H$ spectrum in $D_2O$ indicates the presence of two β-furyl protons at $\delta = 6.46$ and 6.78 and the absence of the α-furyl proton. The negative ion mass spectrum ($NH_3$) show a peak at 148 corresponding to the furylsulfonate sub-unit.

All the isolated salts are stable but hygroscopic and must be handled rapidly under ambient conditions. The water solubility of our new phosphanes is given in Table 1. Three observations can be made. The water-solubilizing effects of the sulfinate and carboxylate functionalities are almost identical. Compounds **12**, **16**, and **19** display a water solubility in the same range as that of the classical TPPTS ligand (1100−1200 g·L$^{-1}$ at 20 °C). Finally, the synergistic effect of furan is quite obvious. The water solubility of $Ph_2P-C_6H_4-PO_3Na_2$, only 300−400 g·L$^{-1}$ according to Stelzer and coll.,[6d] may be compared with 680 g·L$^{-1}$ for **14**.

The synthetic study was completed by a preliminary investigation of the catalytic potential of our new water-soluble furylphosphanes. The selected reactions were: (a) the hydrogenation of (*Z*)-α-acetamidocinnamic acid, (b) the hydroformylation of styrene with rhodium (I) and (c) a Heck cross-coupling reaction with palladium (0) (Scheme 6).

The results are summarized in Table 2, Table 3 and Table 4. Inspection of the Tables shows that the sulfinates are rather disappointing ligands for hydrogenation and Heck coupling. In both cases, the sulfinate appears to poison the catalyst. This inhibiting effect is most marked for hydrogenation. Also noteworthy is the fact that the trifunctional products **12** and **19** display a sharp drop in activity compared to the corresponding mono- **4**, **17** and difunctional **11**, **18** products. A very high solubility in water here seems to be detrimental. By contrast, the ligand which performs best is the phosphonate **14** ($Na^+$). For the Heck coupling, a complete conversion is achieved in 2 h at




Scheme 6. Selected catalytic reactions

Table 2. Hydrogenation of (*Z*)-α-acetamidocinnamic acid

| Ligand[a] | $H_2$ pressure [bars] | Time [h] | Conversion [%] |
|---|---|---|---|
| **1** | 3.3 | 2.5 | 100 |
| **4** ($Na^+$) | 4.0 | 4.5 | 95 |
| **11** ($Li^+$) | 3.8 | 3 | 82 |
| **12** ($Li^+$) | 3.4 | 3 | 100 |
| **14** ($Na^+$) | 3.1 | 2 | 100 |
| **16** ($Na^+$) | 3.1 | 2 | 100 |
| **17** ($Na^+$) | 3.0 | 2 | 0 |
| **18** ($Li^+$) | 3.5 | 3 | 0 |
| **19** ($Li^+$) | 3.5 | 3 | 0 |

[a] Catalyst: $[Rh(COD)_2][PF_6]$ + 2L (1.25%); medium: methanol/water 1:1 at 23 °C.

Table 3. Hydroformylation of styrene

| Ligand[a] | Temp. [°C] | Time [h] | Conversion [%] | Linearity [%] |
|---|---|---|---|---|
| **4** ($Na^+$) | 50 | 23 | 74 | 26 |
| **11** ($Li^+$) | 50 | 17 | 89 | 36 |
| **12** ($Li^+$) | 50 | 17 | 27 | 27 |
| **14** ($Na^+$) | 65 | 18 | 100 | 17 |
| **16** ($Na^+$) | 55 | 18 | 65 | 29 |
| **17** ($Na^+$) | 50 | 18 | 69 | 19 |
| **18** ($Li^+$) | 50 | 17 | 79 | 26 |
| **19** ($Li^+$) | 50 | 17 | 87 | 26 |
| TPPTS | 50 | 18 | 74 | 26 |

[a] Catalyst: $[Rh(CO)_2(acac)]$ + 2L (0.4%); medium: toluene/water 1:1; styrene concentration: 100 g·L$^{-1}$; $H_2$/CO: 1:1, 20 bars.

40 °C, whereas only a 21% conversion is obtained with TPPTS under the same conditions. Similarly in hydroformylation, a better ratio of branched aldehyde is obtained

Table 4. Heck coupling between iodobenzene and ethyl acrylate

| Ligand[a] | Temp. [°C] | Time [h] | Conversion [%] |
|---|---|---|---|
| **4** ($Na^+$) | 22 | 2 | 3 |
| | 40 | 2 | 55 |
| | 80 | 1 | 90 |
| **11** ($Li^+$) | 22 | 17 | 67 |
| | 40 | 2 | 99 |
| | 70 | 1 | 100 |
| **12** ($Li^+$) | 40 | 2 | 12 |
| | 80 | 1 | 30 |
| **14** ($Na^+$) | 40 | 2 | 100 |
| | 70 | 1 | 100 |
| **16** ($Na^+$) | 40 | 1 | 28 |
| | 80 | 1 | 93 |
| **18** ($Li^+$) | 22 | 10 | 65 |
| | 40 | 4 | 40 |
| | 80 | 2.5 | 100 |
| **19** ($Li^+$) | 40 | 2 | 0 |
| | 80 | 1 | 0 |
| TPPTS | 40 | 2 | 21 |
| | 70 | 1 | 100 |

[a] Catalyst: $[Pd(Oac)_2]$ + 3L (2.5%) + excess $Et_3N$; Medium: $CH_3CN$/water 6:1.

from styrene with **14** ($Na^+$) than with TPPTS: 83 *versus* 74%. It has already been noted that triphenylphosphane-phosphonates perform well in Pd-catalyzed carbonylation of benzyl chloride[12] and in Suzuki cross-coupling reactions.[13] 1-Phosphononorbornadiene-phosphonates also perform well in rhodium-catalyzed hydrogenation and hydroformylation provided that the phosphonate group is located on the β-position in order to prevent the chelation of rhodium by the P=O.[6c] More work is obviously required to fully evaluate the catalytic potential of **14**.

## Conclusion

The choice of the furan ring for assembling water-soluble phosphanes was initially suggested by the observation of the increasingly greater use of tris-furylphosphane as ligand in homogeneous catalysis and by a suspected synergistic effect of the furyl group upon water-solubility. This last expectation has been fully substantiated by the experimental observations. Monofunctional derivatives such as **4** and **14** display a water-solubility close to that of the corresponding difunctional derivatives in the analogous phenyl series. Taking into account the preliminary test on some representative catalytic reactions, ligand **14** appears to be a promising addition to the array of water-soluble phosphanes for biphasic catalysis. The synthetic technique involving a selective α-metallation of the furan ring allows the straightforward preparation of the products which are practically pure and may be used directly. From that standpoint, this technique is easier to use on the laboratory scale than the widely used method employed for the preparation of the of the phenyl ring counterparts as exemplified by the synthesis of TPPTS. No special precautions are needed to avoid oxidation of the trivalent phosphanes.

## Experimental Section

**General Remarks:** NMR spectra were recorded with a Bruker AC200 SY spectrometer operating at 200.13 MHz for $^1$H, 50.32 MHz for $^{13}$C and 81.01 MHz for $^{31}$P. Chemical shifts are expressed in ppm downfield from internal TMS ($^1$H and $^{13}$C) or external 85% $H_3PO_4$ ($^{31}$P). Mass spectra were obtained at 70 eV with a Hewlett Packard 5890 gas spectrometer with an SGE BPX (25M × 0.22 mm) column using splitless injection and a helium gas vector at 1 mL/min, coupled with a Hewlett Packard 5989 B mass spectrometer. Elemental analyses were performed by the " Service d'analyse du CNRS " at Gif-sur-Yvette, France. All melting points are uncorrected. Organic solvents were purified by standard procedures. THF was distilled under an inert atmosphere from purple solutions of sodium benzophenone ketyl. The synthesis of all compounds were carried out under dry nitrogen.

**Bis[2-(5-bromofuryl)]phenylphosphane (6):** A solution of LDA (*n*BuLi 1.45 M in hexane, 82.76 mL, 120 mmol and diisopropylamine 12.27 g, 120 mmol) in THF (100 mL) was treated dropwise at −40 °C with a solution of difurylphenylphosphane[14] (9.7 g, 40 mmol) in THF (30 mL). The resulting mixture was stirred for 90 min at −40 °C, then added with a canula to a solution of $BrF_2CCF_2Br$ (31.15 g, 120 mmol) in THF (50 mL). The dark mixture was allowed to warm at room temperature. After acidic hydrolysis with 1.2 N HCl (100 mL), the resulting mixture was extracted with $Et_2O$ (3 × 25 mL). The combined organic phases were dried over $MgSO_4$, filtered and concentrated in vacuo to give a brown oil. Purification by chromatography through a silica plug ($CH_2Cl_2$) afforded an orange oil which crystallized at room temperature (11.0 g, 69% yield). − $^{31}$P NMR ($CDCl_3$): δ = −48.75. − $^1$H NMR ($CDCl_3$): δ = 6.32 (dd, $^3J_{HH}$ = 3.36 Hz, $^4J_{HP}$ = 1.44 Hz, 2 H, $H^4$), 6.70 (dd, $^3J_{HH}$ = 3.26 Hz, $^3J_{HP}$ = 1.77 Hz, 2 H, $H^3$), 7.31−7.50 (m, 5 H, $C_6H_5$). − $^{13}$C NMR ($CDCl_3$): δ = 113.33 (d, $^3J_{CP}$ = 6.00 Hz, $C^4$), 124.92 (d, $^2J_{CP}$ = 22.97 Hz, $C^3$), 127.87 (s, $C^2$), 129.29 (d, $^3J_{CP}$ = 7.60 Hz, $C_{meta}$), 130.02 (s, $C_{para}$), 133.29 (d, $^2J_{CP}$ = 20.14 Hz, $C_{ortho}$), 133.95 (s, $C_{ipso}$), 153.19 (d, $^3J_{CP}$ = 13.80 Hz, $C^5$). − $C_{14}H_9O_2PBr_2$ (400.01): calcd. C 42.04, H 2.27, P 7.74; found C 41.94, H 2.19, P 7.53.

**Tris[2-(5-bromofuryl)]phosphane (7):** A solution of *n*BuLi (1.50 M in hexane, 33.3 mL, 50 mmol) and TMEDA (7.62 mL, 50 mmol) in THF (50 mL) was treated dropwise with stirring at −20 °C with a solution of trifurylphosphane[15] (2.32 g, 10 mmol) in THF (20 mL). After 45 min, a solution of diisopropylamine (2.05 g, 20 mmol) in THF (10 mL) was added at the same temperature. The resulting orange mixture was stirred for an additional 15 min, then added via a canula to a solution of $BrF_2CCF_2Br$ (13 g, 50 mmol) in THF (50 mL), at −60 °C. The mixture was allowed to warm to room temperature and was then hydrolyzed with 1.6 N HCl (50 mL). After extraction with $Et_2O$ (3 × 25 mL), the combined organic extracts were dried over $MgSO_4$, filtered and concentrated in vacuo. The brown solid (4.39 g) obtained was washed with hexane (2 × 30 mL), then filtered through a silica plug (hexane/$CH_2Cl_2$ 50:50) to give **7** as a white solid (3.15 g, 67%), m.p. 108 °C. − $^{31}$P NMR ($CDCl_3$): δ = −75.22. − $^1$H NMR ($CDCl_3$): δ = 6.34 (dd, $^3J_{HH}$ = 3.30 Hz, $^4J_{PH}$ = 1.49 Hz, 3 H, $H^4$), 6.79 (dd, $^3J_{HH}$ = 3.32 Hz, $^3J_{HP}$ = 1.67 Hz, 3 H, $H^3$). − $^{13}$C NMR ($CDCl_3$): δ = 113.51 (d, $^3J_{CP}$ = 6.09 Hz, $C^4$), 124.86 (d, $^2J_{CP}$ = 22.87 Hz, $C^3$), 128.09 (s, $C^2$), 150.73 (d, $^3J_{CP}$ = 4.25 Hz, $C^5$). − MS: *m/z* (%) = 468 (7)[$M^+$], 389 (41) [M − Br], 308 (20) [M − 2Br], 280 (40), 201 (100), 173 (86). − $C_{12}H_6O_3PBr_3$ (468.87): calcd. C 30.74, H 1.29, P 6.61; found C 30.67, H 1.13, P 6.36.

**Tris-[2-(5-chlorofuryl)]phosphane (10):** The experimental protocol was the same as for **7**. Hexachloroethane (40 mmol) was used as

the chlorinating agent. The resulting crude brown oil was filtered through a silica plug (hexane/$CH_2Cl_2$ 1:1) to give **10** as a white solid (77%), m.p. 78 °C. – $^{31}$P NMR ($CDCl_3$): δ = −75.49. – $^1$H NMR ($CDCl_3$): δ = 6.19 (dd, $^3J_{HH}$ = 3.30 Hz, $^4J_{HP}$ = 1.55 Hz, 3 H, $H^4$), 6.82 (dd, $^3J_{HH}$ = 3.32 Hz, $^3J_{HP}$ = 1.85 Hz, 3 H, $H^3$). – $^{13}$C NMR ($CDCl_3$): δ = 108.48 (d, $^3J_{CP}$ = 5.99 Hz, $C^4$), 124.66 (d, $^2J_{CP}$ = 23.13 Hz, $C^3$), 142.20 (d, $^1J_{CP}$ = 2.80 Hz, $C^2$), 148.37 (d, $^3J_{CP}$ = 4.51 Hz, $C^5$). – $C_{12}H_6O_3PCl_3$ (335.51): calcd. C 42.96, H 1.80, P 9.23; found C 43.01, H 1.67, P 9.11.

**General Procedure for the Preparation of Compounds 3, 11 and 12:** A 500 mL four-necked round-bottomed flask fitted with a low temperature thermometer, a mechanical stirrer, a dropping funnel, a nitrogen inlet and a bubbler was charged with a solution of *n*BuLi (1.55 M in hexane, 30.3 mL, 47 mmol for compound **3**; 1.45 M, 34.48 mL, 50 mmol for compound **11**; 1.52 M, 29.7 mL, and 45 mmol for compound **12**) in THF (100 mL). A solution of the appropriate phosphane (diphenylfurylphosphane **1**,[16] 10.65 g, 42.3 mmol for compound **3**; phosphane **6**, 10.0 g, 25 mmol for compound **11**; phosphane **7**, 6.9 g, 15 mmol for compound **12**) in THF (50 mL) was then added dropwise at room temperature for the diphenylfurylphosphane, (compound **3**) or at −80 °C for the bromofurylphosphanes **6** and **7** (compounds **11**, **12**). The resulting orange mixture was stirred for a further 30 min at the same temperature. The anion in suspension was then added via a canula to a Dewar containing an excess of crushed $CO_2$ in $Et_2O$. The mixture was left overnight to effect slow degassing. The solvents were then evaporated and the residue taken to dryness to give white powders.

**Sodium 5-(Diphenylphosphanyl)-furyl-2-carboxylate (4):** The crude product **3** in $Et_2O$ was dissolved in $NaHCO_3$ aq., cooled in an ice bath then carefully acidified with small amounts of 12 N HCl until pH neutral with magnetic stirring. The product was extracted with $CH_2Cl_2$ (3 × 25 mL). The combined organic phases were dried over $MgSO_4$, filtered and evaporated to dryness. The stoichiometric amount of NaOH was then added to a solution of the phosphane in $CH_2Cl_2$ at 0 °C. The solvents were evaporated and the residue triturated with $Et_2O$. The salt was taken to dryness in vacuo to give a white powder (85%), m.p. >190 °C (dec.). – $^{31}$P NMR ($D_2O$): δ = −25.15. – $^1$H NMR ($D_2O$): δ = 6.20 (d, $^3J_{HH}$ = 3.16 Hz, 1 H, $H^4$), 6.81 (dd, $^3J_{HH}$ = 3.23 Hz, $^3J_{HP}$ = 1.20, 1 H, $H^3$), 6.90−7.20 (m, 10 H, 2 × $C_6H_5$). – $^{13}$C NMR ($D_2O$): δ = 117.78 (s, $C^4$), 124.89 (d, $^2J_{CP}$ = 8.00 Hz, $C^3$), 131.09 (d, $^3J_{CP}$ = 7.01 Hz, $C_{meta}$), 131.73 (s, $C_{para}$), 135.47 (d, $^2J_{CP}$ = 19.69 Hz, $C_{ortho}$), 136.81 (d, $^1J_{CP}$ = 4.35 Hz, $C_{ipso}$), 156.36 (s, $C^5$), 156.94 (d, $^1J_{CP}$ = 13.72 Hz, $C^2$), 168.14 (s, $CO_2$).

**Lithium 5-Phenylphosphanyl-bis(furyl-2-carboxylate) (11):** 89% yield, m.p. >270 °C. – $^{31}$P NMR ($D_2O$): δ = −48.33. – $^1$H NMR ($D_2O$): δ = 6.51 (dd, $^4J_{HP}$ = 1.33 Hz, $^3J_{HH}$ = 3.38 Hz, 2 H, $H^4$), 6.85 (dd, $^3J_{HP}$ = 1.23 Hz, $^3J_{HH}$ = 3.27 Hz, 2 H, $H^3$), 7.15 (m, 5 H, $C_6H_5$). – $^{13}$C NMR ($D_2O$): δ = 116.46 (d, $^3J_{CP}$ = 4.81 Hz, $C^4$), 124.13 (d, $^2J_{CP}$ = 22.34 Hz, $C^3$), 129.80 (d, $^3J_{CP}$ = 7.56 Hz, $C_{meta}$), 130.68 (s, $C_{para}$), 133.31 (s, $C_{ipso}$), 133.51 (d, $^2J_{CP}$ = 20.16 Hz, $C_{ortho}$), 152.77 (d, $^1J_{CP}$ = 11.65 Hz, $C^2$), 155.00 (s, $C^5$), 166.68 (s, $CO_2$).

**Lithium 5-Phosphanyl-tris-(furyl-2-carboxylate) (12):** 87% yield, m.p. >270 °C. – $^{31}$P NMR ($D_2O$): δ = −72.21. – $^1$H NMR ($D_2O$): δ = 6.91 (dd, $^4J_{HP}$ = 0.85 Hz, $^3J_{HH}$ = 3.45 Hz, 3 H, $H^4$), 6.96 (dd, $^3J_{HP}$ = 1.15 Hz, $^3J_{HH}$ = 3.50 Hz, 3 H, $H^3$). – $^{13}$C NMR ($D_2O$): δ = 116.46 (d, $^3J_{CP}$ = 5.07 Hz, $C^4$), 123.91 (d, $^2J_{CP}$ = 18.76 Hz, $C^3$), 150.62 (s, $C^5$), 154.82 (d, $^1J_{CP}$ = 4.41 Hz, $C^2$), 166.69 (s, $CO_2$).

**General Procedure for the Preparation of Compounds 13 and 15:** The same reactor as above was charged with a solution of *n*BuLi (1.45 M in hexane, 13.8 mL, 20 mmol for compound **13**), (1.55 M in hexane, 42 mL, 65 mmol for compound **15**), in THF (30−50 mL). The mixture was cooled to 0 °C then TMEDA (2.35 g, 20 mmol or 7.04 g, 60 mmol) was added rapidly. After 5 min, a solution of furan (1.44 g, 21 mmol for compound **13**), (4.13 g, 60 mmol for compound **15**) in THF (10−50 mL) was added dropwise and the mixture was stirred at 0 °C for 30 min. The mixture was then cooled to −60 °C and a solution of chlorodiphenylphosphane (4.55 g, 20 mmol) or dichlorophenylphosphane (5.54 g, 30 mmol) in THF (20−30 mL) was added dropwise. The reaction mixture was allowed to warm to room temperature and stirred for a further 2 h. The formation of furylphosphane was monitored by $^{31}$P NMR spectroscopy. The reaction mixture was then cooled to −20 °C and treated dropwise and successively with a second equivalent of *n*BuLi, TMEDA in THF (20−50 mL). The resulting orange mixture was stirred for 30 min and then added dropwise via a canula to a second 500 mL round-bottomed flask charged with freshly distilled chlorodiethylphosphate (3.56 g, 20 mmol or 10.67 g, 60 mmol) in THF (30 mL) at −78 °C. Then the mixture was allowed to warm to room temperature and hydrolyzed with a saturated aqueous solution of $NH_4Cl$ (50−100 mL). The mixture was extracted with $Et_2O$ (3 × 25 mL), the combined organic phases dried over $MgSO_4$, filtered and the solvents removed in vacuo. The colored oil was warmed in a Kügelrohr apparatus to eliminate the phosphate side-products and purified by chromatography with ethyl acetate.

**2-(5-Diethoxyphosphonofuryl)diphenylphosphane (13):** 70% yield. – $^{31}$P NMR ($CDCl_3$): δ = −26.74 (s, $P^{III}$), −2.60 (s, $P$=O). – $^1$H NMR ($CDCl_3$): δ = 1.23 (dt, $^4J_{HP}$ = 0.50 Hz, $^3J_{HH}$ = 7.04 Hz, 6 H, 2 × $CH_3$), 4.07 (mq, $^3J_{HP}$ = 0.82 Hz, $^3J_{HH}$ = 7.06 Hz, 4 H, 2 × $CH_2$), 6.58 (m, 1 H, $C^4$−$H$), 7.15 (m, 1 H, $C^3$−$H$), 7.27−7.43 (m, 10 H, 2 × $C_6H_5$). – $^{13}$C NMR ($CDCl_3$): δ = 16.73 (d, $^3J_{CP}$ = 6.67 Hz, $CH_3$), 63.56 (d, $^2J_{CP}$ = 5.20 Hz, $CH_2$), 121.62 (dd, $J_{CP}$ = 10.95 Hz, $J_{CP}$ = 18.38 Hz, $C^4$), 123.99 (dd, $J_{CP}$ = 3.74 Hz, $J_{CP}$ = 25.09 Hz, $C^3$), 129.17 (d, $^3J_{CP}$ = 7.41 Hz, $C_{meta}$), 129.85 (s, $C_{para}$), 134.02 (d, $^2J_{CP}$ = 19.86 Hz, $C_{ortho}$), 135.52 (d, $^1J_{CP}$ = 6.09 Hz, $C_{ipso}$), 149.32 (d, $^1J_{CP}$ = 234.92 Hz, $C^5$), 160.57 (dd, $J_{CP}$ = 8.39 Hz, $J_{CP}$ = 22.13 Hz, $C^2$). – $C_{20}H_{22}O_4P_2$ (388.34): calcd. C 61.86, H 5.71, P 15.95; found C 61.82, H 5.69, P 15.86.

**Bis[2-(5-diethoxyphosphonofuryl)]phenylphosphane (15):** 40% yield. – $^{31}$P NMR ($CDCL_3$): δ = −47.64 (s, $P^{III}$), 2.76 (s, $P^V$). – $^1$H NMR ($CDCL_3$): δ = 1.23 (dt, $^4J_{HP}$ = 0.50 Hz, $^3J_{HH}$ = 7.04 Hz, 12 H, 4 × $CH_3$), 4.07 (mq, $^3J_{HP}$ = 0.82 Hz, $^3J_{HH}$ = 7.06 Hz, 8 H, 4 × $CH_2$), 6.58 (m, 2 H, 2 × $C^4$−$H$), 7.15 (m, 2 H, 2 × $C^3$−$H$), 7.27−7.43 (m, 5 H, $C_6H_5$). – $^{13}$C NMR ($CDCl_3$): δ = 16.73 (d, $^3J_{CP}$ = 6.67 Hz, $CH_3$), 63.56 (d, $^2J_{CP}$ = 5.20 Hz, $CH_2$), 121.62 (dd, $J_{CP}$ = 10.95 Hz, $J_{CP}$ = 18.38 Hz, $C^4$), 123.99 (dd, $J_{CP}$ = 3.74 Hz, $J_{CP}$ = 25.09 Hz, $C^3$), 129.17 (d, $^3J_{CP}$ = 7.41 Hz, $C_{meta}$), 129.85 (s, $C_{para}$), 134.02 (d, $^2J_{CP}$ = 19.86 Hz, $C_{ortho}$), 135.52 (d, $^1J_{CP}$ = 6.09 Hz, $C_{ipso}$), 149.32 (d, $^1J_{CP}$ = 234.92 Hz, $C^5$), 160.57 (dd, $J_{CP}$ = 8.39 Hz, $J_{CP}$ = 22.13 Hz, $C^2$). – $C_{22}H_{29}O_8P_3$ (514.39): calcd. C 51.37, H 5.68, P 18.06; found C 51.29, H 5.63, P 18.03.

**General Procedure for the Preparation of Compounds 14 and 16:** A solution of **13** (11.18 g, 28.8 mL) or **15** (8.55 g, 16.6 mL) in $CH_2Cl_2$ (50 mL) stirred magnetically at 5 °C was treated dropwise with $BrSiMe_3$ (8 mL, 60 mmol or 9.43 mL, 70 mmol). The mixture was stirred until $^{31}$P NMR spectroscopy indicated complete silylation (typically 4 h). The solvents were evaporated and the oily residue dissolved in acetone (50 mL). Water (1.5−2 mL) was then added and the mixture stirred for 3 h. The reaction mixture was evaporated to dryness and the solid residue redissolved in MeOH (50 mL). Sodium hydroxide (2.37 g, 57.5 mmol or 2.72 g, 66 mmol)

was added in portions with stirring. The precipitated white solid was dried (90 °C/ 0.01 Torr) until constant weight; 7.64 g for compound **14** (71%) and 6.7 g for compound **16** (82%).

**Sodium (5-Diphenylphosphanyl)-2-furylphosphonic acid (14):** M.p. >270 °C. − $^{31}$P NMR ($D_2O$): δ = −27.69 (s, $P^{III}$), −0.06 (s, $P$=O). − $^{1}$H NMR ($D_2O$): δ = 6.66 (pseudo quint, 1 H, $^{3}J_{HH}$ = 3.20 Hz, $^{4}J_{HP}$ = $^{3}J_{HOP}$ = 1.60 Hz, $C^4$ *H*), 6.75 (pseudo quint, 1 H, $^{3}J_{HH}$ = 3.26 Hz, $^{3}J_{HP}$ = $^{4}J_{HOP}$ = 1.62 Hz, $C^3$ *H*), 7.43−7.53 (m, 10 H, 2 × $C_6H_5$). − $^{13}$C NMR ($D_2O$): δ = 117.50 (d, $J_{CP}$ = 19.79 Hz, $C^4$), 124.72 (d, $J_{CP}$ = 24.11 Hz, $C^3$), 131.32 (d, $^{3}J_{CP}$ = 7.29 Hz, $C_{meta}$), 131.88 (s, $C_{para}$), 135.56 (d, $^{2}J_{CP}$ = 19.18 Hz, $C_{ortho}$), 137.66 (s, $C_{ipso}$), 154.56 (d, $^{1}J_{CP}$ = 6.63 Hz, $C^2$), 164.90 (d, $^{1}J_{CPO}$ = 198.46 Hz, $C^5$).

**Sodium (5-Phenylphosphanyl)-bis(2-furylphosphonic acid) (16):** M.p. >270 °C. − $^{31}$P NMR ($D_2O$): δ = −49.54 (s, $P^{III}$), −0.02 (s, 2 × $P$=O). − $^{1}$H NMR ($D_2O$): δ = 6.67 (pseudo P, Σ $J_{HP}$ = 5.94 Hz, 2 H, $C^4$ *H*), 6.80 (pseudo sext, Σ $J_{HP}$ = 5.72 Hz, 2 H, $C^3$ *H*), 7.36−7.51 (m, 5 H, $C_6H_5$). − $^{13}$C NMR ($D_2O$): δ = 117.66 (d, $J_{CP}$ = 20.43 Hz, $C^4$), 123.89 (dd, $J_{CP}$ = 9.15 Hz, $J_{CP}$ = 18.31 Hz, $C^3$), 131.36 (d, $^{3}J_{CP}$ = 7.03 Hz, $C_{meta}$), 131.87 (s, $C_{para}$), 134.67 (d, $^{2}J_{CP}$ = 18.97 Hz, $C_{ortho}$), 136.95 (s, $C_{ipso}$), 153.49 (d, $^{1}J_{CP}$ = 7.29 Hz, $C^2$), 164.54 (d, $^{1}J_{CPO}$ = 199.55 Hz, $C^5$).

**General Procedure for the Preparation of Compounds 17−19:** The same reactor as above was charged with a solution of *n*BuLi (1.52 M in hexane, 19.8 mL, 30 mmol) in THF (50 mL). A solution of the appropriate phosphane in THF (20 mL) was then added dropwise at room temperature for the diphenylfurylphosphane **1** (compound **17**) or at −80 °C for the bromofurylphosphanes **6**, **7** (compounds **18**, **19**). The resulting orange mixture was stirred for a further 30 min at −60 °C before the nitrogen atmosphere was replaced by a slow stream of $SO_2$. The temperature must be carefully maintained at −60 °C since the reaction is strongly exothermic. The flow of $SO_2$ was stopped when no more precipitation of the sulfinate was observed or when the mixture became vivid yellow. Nitrogen was then bubbled into the mixture for an hour at −60 °C and the mixture then allowed to warm slowly to room temperature. The slightly yellow precipitate was filtered, washed with $Et_2O$ (3 × 50 mL) then taken to dryness in vacuo to give a pale yellow powder.

**Sodium (5-Diphenylphosphanyl)-2-furylsulfinic Acid (17):** The crude product in $Et_2O$ was extracted with $H_2O$ (3 × 50 mL). The combined aqueous phases were cooled at 5 °C and $CH_2Cl_2$ (100 mL) added. The stirred mixture was acidified with 3 N HCl (10 mL) then extracted with $CH_2Cl_2$ (2 × 25 mL). The combined organic phases were cooled to 5 °C and treated with an equivalent of NaOH. The solvents were evaporated and the residue triturated with $Et_2O$. The salt was taken to dryness in vacuo to give a white powder (6.86 g, 68%), m.p. 170 °C (dec.). − $^{31}$P NMR ($D_2O$): δ = −26.67. − $^{1}$H NMR ($D_2O$): δ = 6.41 (dd, $^{3}J_{HH}$ = 3.37 Hz, $^{4}J_{HP}$ = 1.47 Hz, 1 H, $C^4$ *H*), 6.54 (dd, $^{3}J_{HH}$ = 3.38 Hz, $^{3}J_{HP}$ = 1.19 Hz, 1 H, $C^3$ *H*), 6.90−7.20 (m, 10 H, 2 × $C_6H_5$). − $^{13}$C NMR ($D_2O$): δ = 111.59 (s, $C^4$), 124.83 (s, $C^3$), 131.06 (d, $^{3}J_{CP}$ = 6.92 Hz, $C_{meta}$), 131.70 (s, $C_{para}$), 135.45 (d, $^{2}J_{CP}$ = 19.44 Hz, $C_{ortho}$), 136.92 (d, $^{1}J_{CP}$ = 2.90 Hz, $C_{ipso}$), 156.58 (d, $^{1}J_{CP}$ = 16.50 Hz, $C^2$), 170.05 (s, $C^5$).

**Lithium (5-Phenylphosphanyl)-bis(2-furylsulfinic acid) (18):** M.p. 190 °C (dec.). − $^{31}$P NMR ($D_2O$): δ = −48.14. − $^{1}$H NMR ($D_2O$): δ = 6.67 (pseudo quint, Σ $J_{HP}$ = 6.02 Hz, 2 H, $C^4$ *H*), 6.82 (pseudo p, Σ $J_{HP}$ = 5.87 Hz, 2 H, $C^3$ *H*), 7.35−7.43 (m, 5 H, $C_6H_5$). − $^{13}$C NMR ($D_2O$): δ = 111.83 (d, $^{3}J_{CP}$ = 4.58 Hz, $C^4$), 125.00 (d, $^{2}J_{CP}$ = 21.36 Hz, $C^3$), 131.32 (d, $^{3}J_{CP}$ = 7.63 Hz, $C_{meta}$), 132.13 (s, $C_{para}$), 134.90 (d, $^{2}J_{CP}$ = 19.84 Hz, $C_{ortho}$), 135.28 (s, $C_{ipso}$), 154.26 (d, $J_{CP}$ = 9.16 Hz, $C^2$), 170.00 (s,$C^5$).

**Lithium (5-Phosphanyl)-tris-(2-furylsulfinic acid) (19):** M.p. 240 °C (dec.). − $^{31}$P NMR ($D_2O$): δ = −72.55. − $^{1}$H NMR ($D_2O$): δ = 6.64 (dd, $^{4}J_{HP}$ = 1.34 Hz, $^{3}J_{HH}$ = 3.45 Hz, 3 H, $C^4$ *H*), 6.88 (dd, $^{3}J_{HP}$ = 1.03 Hz, $^{3}J_{HH}$ = 3.44 Hz, 3 H, $C^3$ *H*). − $^{13}$C NMR ($D_2O$): δ = 110.36 (d, $^{3}J_{CP}$ = 5.94 Hz, $C^4$), 123.34 (d, $^{2}J_{CP}$ = 19.96 Hz, $C^3$), 150.56 (d, $^{1}J_{CP}$ = 3.23 Hz, $C^2$), 168.39 (s, $C^5$).

**General Procedure for the Hydrogenation Reaction:** The catalyst $[Rh(COD)_2][PF_6]$ (11.6 mg, 0.025 mmol, 1.25 mol-%) was dissolved in a Schlenk tube in 1 mL of acetone. A solution of phosphane (2.5 mol-%) dissolved in 1 mL of water was then added dropwise to the orange mixture with magnetic stirring and under argon. The resulting yellow solution was checked by $^{31}$P NMR spectroscopy, and then injected into a 50 mL stainless steel autoclave containing a mixture of (*Z*)-α-acetamido cinnamic acid in acetone (15 mL) and $H_2O$ (15 mL). The reactor was pressurized to 3.0−3.6 bars of $H_2$ and magnetically stirred at room temperature for 2−3 h. The crude reaction mixture was concentrated in vacuo then analyzed by $^{1}$H NMR spectroscopy in [$D_6$]DMSO solution.

**General Procedure for the Hydroformylation of Styrene:** The catalyst $[Rh(acac)(CO)_2]$ (10.13 mg, 0.04 mol, 0.4 mol-%) was dissolved in toluene (1 mL) in a Schlenk tube. The phosphane dissolved in $H_2O$ (1 mL) was added dropwise, and the resulting mixture kept under argon for a few minutes until the color of the organic layer was discharged.

A 250 mL stainless steel autoclave magnetically stirred was charged with styrene (1.0 g, 9.6 mmol), toluene (2.5 mL), $H_2O$ (2.5 mL) and then with the previously prepared catalyst solution. The reactor was pressurized to 20 bars with 10 bars of CO and 10 bars of $H_2$, and heated in a thermostatic bath at 50 °C. The crude reaction mixtures were analyzed by GLC to determine the conversion and the selectivity of the reaction.

**General Procedure for the Catalytic Heck Reaction:** In a Schlenk tube equipped with a magnetic bar, iodobenzene (0.42 g, 2 mmol), EtOAc (0.30 g, 3 mmol) and triethylamine (0.31 g, 3 mmol) were dissolved in acetonitrile/water (6:1) solution (3.5 mL). The phosphane (7.5 mol-%) and $Pd(OAc)_2$ (2.5 mol-%) were quickly poured into the Schlenk tube and the mixture stirred vigorously, at the required temperature. The reaction mixture was treated with water and extracted with $Et_2O$. The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo. The resulting crude product was then analyzed by gas chromatography (GLC).

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