DOI: 10.1002/ejoc.200901407

*n*BuLi-Mediated Hydrophosphination: A Simple Route to Valuable Organophosphorus Compounds

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Keywords: Alkenes / Alkynes / Hydrophosphination / Ligand design / Phosphorus

A straightforward synthesis of homoallyl- and allylphosphanes has been developed using *n*BuLi-mediated hydrophosphination of conjugated dienes. In all the cases the phosphorus atom of the reacting phosphane attacked the sterically less demanding side of the diene exclusively. In addition, high regioselectivities towards 1,2- or 1,4-addition products were observed depending on the nature of the dienes. This hydrophosphination reaction was extended to a variety of substrates such as styrene derivatives, alkynes and 1,3,5-cycloheptatriene. The structures of three hydrophosphination products were confirmed by X-ray diffraction studies.

Introduction

Alkenylphosphanes are a promising class of ligand precursors for catalysis.[1] Indeed, these mixed bidentate ligands can lead to stable but nonetheless highly active catalytic systems thanks to the combination of two electronically different binding sites in a single ligand framework and to the presumed lability of the C–C double bond, which can readily and reversibly dissociate from the active metal centre. Thus, there is considerable interest in developing facile and efficient syntheses of these ligands. Alkenylphosphanes can be readily prepared by nucleophilic substitution using either phosphide anions or halogenophosphanes. An alternative atom-economic route towards these compounds involves the hydrophosphination of alkynes and conjugated dienes to form either vinyl-, allyl- or homoallylphosphanes.[2] These reactions can be achieved under radical activation,[3] in basic conditions[4] or alternatively in the presence of group 2,[5] late-transition-metal[6] and lanthanide-based[7] catalysts. The use of phosphane–borane complexes under neutral conditions has also been described.[8] However, most of the above-mentioned reactions suffer from certain limitations, such as the availability of catalysts, the narrow scope of substrates and a lack of selectivity. We report herein a simple and efficient base-promoted hydrophosphination of a variety of 1,3-dienes using several phosphanes and yielding alkenylphosphanes with high regioselectivities. Moreover, this simple procedure has been applied to alkynes, unactivated olefins and cyclo-1,3,5-heptatriene.

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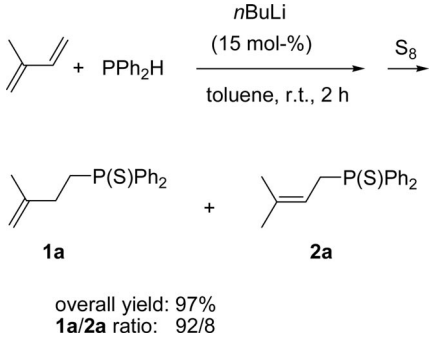
Results and Discussion

We recently described the first titanium-catalysed 1,4-hydrophosphination of conjugated dienes, which afforded allylphosphanes in good yields and regioselectivities.[9]

Searching for ways to improve this process, we noticed that the presence of an excess of *n*BuLi, originally used as a catalyst activator, reduced the regioselectivity of the reaction leading to a mixture of 1,2- and 1,4-addition products. We therefore started to explore the hydrophosphination of 1,3-dienes in the sole presence of *n*BuLi. In an initial experiment we carried out the reaction of isoprene with PPh_2H in toluene in the presence of 15 mol-% *n*BuLi (Scheme 1). The reaction mixture was stirred at room temperature and monitored by GC analysis. Surprisingly, no remaining diphenylphosphane was detected after only 2 h. NMR analysis of the products obtained after sulfidation showed that hydrophosphination of isoprene had occurred, leading almost exclusively to the homoallylphosphane sulfide **1a**.



Scheme 1. *n*BuLi-mediated hydrophosphination of isoprene.

This result explains the detrimental effect of an excess of *n*BuLi on the regioselectivity of the titanium-catalysed hydrophosphination reaction,[9] the first highly 1,2-regioselective hydrophosphination of isoprene reported to date.[10] Crystals of **1a** suitable for X-ray measurements were obtained and confirmed the homallylic structure of the phosphane (Figure 1).

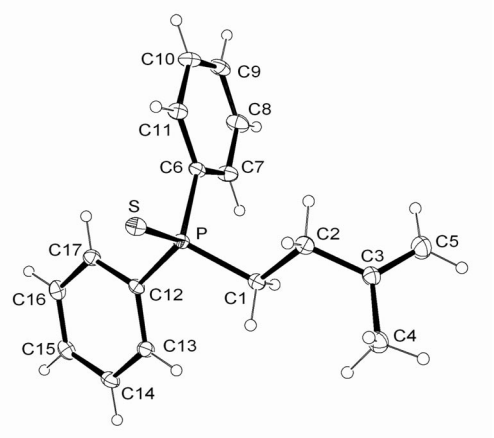
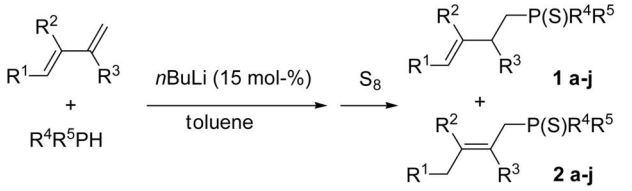


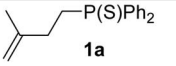
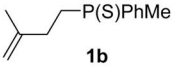
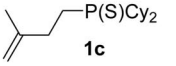
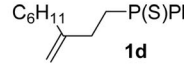
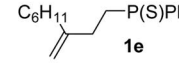
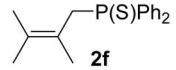
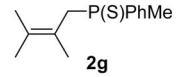
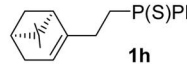
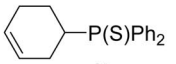
Figure 1. Molecular structure of the homoallylphosphane sulfide **1a**.

Different solvents were then screened and toluene proved to be the best as addition of PPh_2H to isoprene in the presence of 15 mol-% *n*BuLi took place in Et_2O, THF and DMSO but with lower regioselectivities (**1a/2a** ratio 81:19, 72:28 and 51:49, respectively). The same reaction performed in hexane resulted in no conversion. Experiments in ionic liquids such as 1-butyl-2,3-dimethylimidazolium bis-triflimide [BDMIM][NTf_2][11] were also not convincing (low yields and selectivities). In addition, hydrophosphination of isoprene was completed in 1 h at 70 °C but with the opposite regioselectivity (**1a/2a** ratio: 40:60).[12] Thus, detrimental effects of solvent polarity and of reaction temperature on the regioselectivity of the hydrophosphination reaction were observed. These results might be explained on the basis that polar solvents stabilize the ionic intermediates, which favours the thermodynamic 1,4-addition product, as does high temperatures. Note that attempts to reduce or to increase the amount of *n*BuLi (5–40 mol-%) rendered the reaction slower. Finally, the use of a stoichiometric amount of *n*BuLi led to no conversion as was reported in the parent *n*BuLi-mediated hydroamination reaction.[14] After showing that the initial experimental conditions were indeed the best, we explored the scope of the *n*BuLi-mediated hydrophosphination reaction with a variety of dienes and phosphanes (Table 1).

As highlighted in Table 1, all the hydrophosphination products were obtained in high yields. The electron-rich methylphenyl- and dicyclohexylphosphanes participated in the hydrophosphination of isoprene although the reactions rates were somewhat slower (entries 1–3). The regioselectivities reached in these reactions were high and similar to those obtained with PPh_2H. Hydrophosphination of myrcene with PPh_2H and PPhMeH was facile and gave the

Table 1. *n*BuLi-mediated hydrophosphination of a variety of dienes and phosphanes.[a]



Entry	Diene	Product	*T* / time	Yield / **1**:**2** *ratio*
1	isoprene	 **1a**	r.t. / 2 h	97% / *92/8*
2	isoprene	 **1b**	r.t. / 6 h	92% / *85/15*
3	isoprene	 **1c**	r.t. / 8 h	93% / *93/7*
4	myrcene	 **1d**	r.t. / 4 h	94% / *90/10*
5	myrcene	 **1e**	r.t. / 10 h	92% / *75/25*
6	2,3-dimethyl-1,3-butadiene	 **2f**	70 °C / 14 h	89% / *0/100*
7	2,3-dimethyl-1,3-butadiene	 **2g**	70 °C / 24 h	90% / *0/100*
8	(1*R*)-nopadiene	 **1h**	70 °C / 16 h	87% / *100/0*
9	1,3-cyclohexadiene	 **1i**	70 °C / 10 h	87% / *55/45*

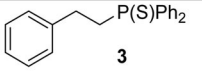
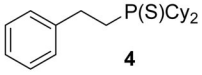
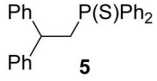
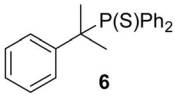
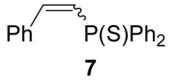
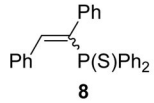
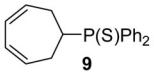
[a] Reaction conditions: toluene (2 mL), phosphane (1.25 mmol), *n*BuLi (0.19 mmol) and diene (3.75 mmol).

homoallylphosphanes **1d** and **1e** in good yields and selectivities (entries 4 and 5). 2,3-Dimethyl-1,3-butadiene required a prolonged reaction time and a higher reaction temperature to go to completion and led exclusively to the allylphosphanes **2f** and **2g** (entries 6 and 7). This opposite regioselectivity can be explained in terms of thermodynamic control taking precedence under these more severe conditions. The use of (1*R*)-nopadiene as a substrate provided a straightforward route to the chiral homoallylphosphane sulfide **1h** (entry 8). Cyclic dienes such as 1,3-cyclohexadiene underwent hydrophosphination at 70 °C but without showing any selectivity (entry 9).

This hydrophosphination reaction was then applied to a variety of C–C multiple bonds (Table 2). The hydrophosphination of styrene with PPh_2H yielded (2-phenylethyl)diphenylphosphane sulfide (**3**) after 16 h at 70 °C and the usual work-up (entry 1). The addition of PCy_2H to styrene under similar conditions afforded the hydrophosphination product **4** in good yield (entry 2). At this point it is worth mentioning that the system *t*BuOK/DMSO allowed this re-

action under milder conditions (room temp., 1 h) but led to the phosphane oxide.[4e] More hindered substrates such as 1,1-diphenylethylene underwent hydrophosphination to give the linear product **5** selectively (entry 3). The opposite regioselectivity was observed by using α-methylstyrene as the substrate (entry 4). This was probably due to the lack of stability of the α-carbanion intermediate such that the phosphide added to the α position instead, creating a more stable primary carbanion at the β position.

Table 2. Substrate scope of the *n*BuLi-mediated hydrophosphination reaction.[a]

Entry	Substrate	Product	*T* time	Yield
1	styrene	 **3**	70 °C 16 h	89%
2	styrene	 **4**	70 °C 24 h	75%[b]
3	1,1-diphenylethylene	 **5**	70 °C 30 h	84%
4	α-methylstyrene	 **6**	70°C 28 h	91%
5	phenylacetylene	 **7**	70 °C 20 h	95%[c]
6	diphenylacetylene	 **8**	70 °C 24 h	93%[c]
7	1,3,5-cycloheptatriene	 **9**	70 °C 18 h	91%

[a] Reaction conditions: toluene (2 mL), phosphane (1.25 mmol), *n*BuLi (0.19 mmol) and substrate (3.75 mmol). [b] The partial telomerization of styrene was observed. [c] *Z*/*E* ratio: 60:40.

Efforts to achieve the hydrophosphination of 1-hexene met with more limited success (6% yield, 3 d, 70 °C). On the other hand, the hydrophosphination reaction could be extended to alkynes;[13] diphenylphosphane added to phenylacetylene in the presence of 15 mol-% *n*BuLi in toluene to give (*Z*)-styryldiphenylphosphane sulfide (**7**) as the main product (entry 5).[15] The *Z* configuration of the major isomer was determined by ^{1}H NMR spectroscopy and confirmed by an X-ray diffraction study. An ORTEP view of **7** is shown in Figure 2.

The reaction of diphenylacetylene under similar conditions afforded the alkenylphosphane **8** in good yield but with modest diastereoselectivity (entry 6).[16] Finally, the use of 1,3,5-cycloheptatriene as the substrate provided (3,5-cycloheptadienyl)diphenylphosphane sulfide (**9**) in excellent yield after the usual work-up (entry 7). Interestingly, no double hydrophosphination product was observed under these conditions. Further, the hydrophosphination of cycloheptatriene could be scaled up to several grams and required no special conditions. The corresponding adduct is

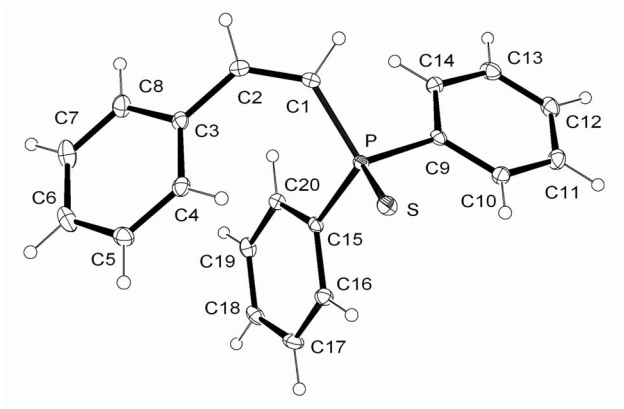


Figure 2. Molecular structure of (*Z*)-styryldiphenylphophane sulfide (**7**).

a solid and was thus easy to isolate as the free phosphane by simple recrystallization of the crude product in pentane. An X-ray diffraction study was performed on suitable crystals and confirmed the structure of the phosphanyldiene (Figure 3). The cycloheptadiene ring exhibits an asymmetrically distorted conformation, as illustrated by the following torsion angles [C1–C2–C3–C4 56.4(4)°, C3–C4–C5–C6 –20.2(6)° and C5–C6–C7–C1 –0.6(5)°] and the diphenylphosphanyl group is located in the *exo* position.

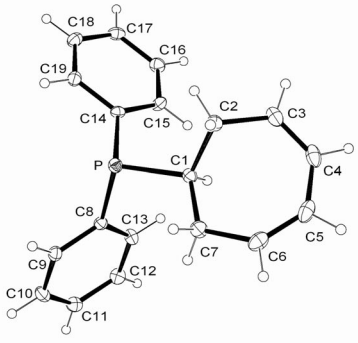


Figure 3. Molecular structure of (3,5-cycloheptadienyl)diphenylphosphane sulfide (**9**).

Conclusions

We have described a simple and efficient method for the hydrophosphination of conjugated dienes mediated by 15 mol-% *n*BuLi. The reactions were applied to a variety of dienes and phosphanes and gave the hydrophosphination products as phosphane sulfides in high yields after sulfidation work-up. The regioselectivity of the process is remarkable. In all cases, the phosphorus atom of the reacting phosphane attacked the sterically less demanding side of the diene exclusively. In addition, high regioselectivities towards 1,2- or 1,4-addition products were observed depending on the nature of the dienes. Finally, this hydrophosphination reaction can be applied to a variety of substrates, such as styrene derivatives, alkynes and 1,3,5-cycloheptatriene.

Most of the phosphanes prepared in this study were isolated as the free phosphanes and readily used as ligands after simple evaporation of the solvent and of the excess diene. Preliminary studies have been carried out specifically with ruthenium complexes and will be published in due course.

Experimental Section

General: All reactions were carried out under purified argon using vacuum line techniques. Solvents were dried and distilled under argon from sodium before use. Elemental analyses were performed with an EA 1108 CHNS-O FISONS Instrument. ^{1}H (300.13 MHz), ^{13}C (75.4 MHz) and ^{31}P (121.13 MHz) NMR spectra were recorded with a Bruker 300 Avance spectrometer. Chemical shifts are quoted in ppm (δ) relative to TMS (^{1}H, ^{13}C) or external H_3PO_4 (^{31}P). Coupling constants are reported in Hz.

Typical Procedure for *n*BuLi-Mediated Hydrophosphination: In a Schlenk tube, a *n*BuLi solution (0.19 mmol, 1.6 M in hexanes) was added to a solution of PR_2H (1.25 mmol) in freshly distilled toluene (2 mL). The solution was stirred for 30 min at room temperature and then the diene (3.75 mmol) was added. The reaction mixture was stirred until full consumption of PR_2H (monitored by GC). S_8 (0.16 mmol) was then added and the reaction mixture was stirred at room temperature for 3 h. The products were purified by silica gel chromatography.

(3-Methyl-3-butenyl)diphenylphosphane Sulfide (1a): White solid (347 mg, 97% yield, m.p. 76 °C). R_f = 0.6 (pentane/Et_2O, 9:1). ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 42.7 (s, PPh_2) ppm. ^{1}H NMR ($CDCl_3$): δ = 1.74 (s, 3 H, =CCH_3), 2.31 (m, 2 H, =CCH_2), 2.60 (m, 2 H, CH_2P), 4.74 (s, 1 H, =CH_2), 4.78 (s, 1 H, =CH_2), 7.44–7.54 (m, 6 H, Ph), 7.82–7.90 (m, 4 H, Ph) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 25.6 (s, 1 C, CH_3), 29.9 (d, $^2J_{CP}$ = 2.3 Hz, 1 C, CH_2), 30.9 (d, $^1J_{CP}$ = 56 Hz, 1 C, CH_2), 110.3 (s, 1 C, =CH_2), 128.7 (d, $^2J_{CP}$ = 11.3 Hz, 4 C, *o*-Ph), 131.1 (d, $^3J_{CP}$ = 9.8 Hz, 4 C, *m*-Ph), 131.5 (d, $^4J_{CP}$ = 3 Hz, 2 C, *p*-Ph), 133.4 (d, $^1J_{CP}$ = 80 Hz, 2 C, *ipso*-Ph), 144.5 (d, $^3J_{CP}$ = 17 Hz, 1 C, *C*=CH_2) ppm. $C_{17}H_{19}PS$ (286.37): calcd. C 71.30, H 6.69, S 11.20; found C 71.15, H 6.77, S 11.53.

(3-Methyl-3-butenyl)(methyl)phenylphosphane Sulfide (1b): Colourless oil (258 mg, 92% yield). R_f = 0.6 (pentane/Et_2O, 9:1). ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 39.7 (s, PMePh) ppm. ^{1}H NMR ($CDCl_3$): δ = 1.71 (s, 3 H, CH_3), 1.95 (d, $^2J_{PH}$ = 12.9 Hz, 3 H, CH_3-P), 2.10 (m, 1 H, CH_2), 2.18–2.28 (m, 2 H, CH_2), 2.37 (m, 1 H, CH_2), 4.69 (s, 1 H, =CH_2), 4.73 (s, 1 H, =CH_2), 7.45–7.60 (m, 3 H, Ph), 7.89–7.93 (m, 2 H, Ph) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 20.8 (d, $^1J_{CP}$ = 56.6 Hz, 1 C, PCH_3), 22.5 (s, 1 C, CH_3), 30.1 (d, $^2J_{CP}$ = 2.3 Hz, 1 C, CH_2), 33.0 (d, $^1J_{CP}$ = 55.1 Hz, 1 C, CH_2), 110.4 (s, 1 C, =CH_2), 128.5 (d, $^2J_{CP}$ = 11.3 Hz, 4 C, *o*-Ph), 130.5 (d, $^3J_{CP}$ = 10.6 Hz, 4 C, *m*-Ph), 131.6 (d, $^4J_{CP}$ = 3 Hz, 2 C, *p*-Ph), 132.2 (d, $^1J_{CP}$ = 77.7 Hz, 2 C, *ipso*-Ph), 144.3 (d, $^3J_{CP}$ = 15.8 Hz, 1 C, *C*=CH_2) ppm. $C_{12}H_{17}PS$ (224.3): calcd. C 64.26, H 7.64, S 14.30; found C 64.64, H 7.81, S 14.62.

(3-Methyl-3-butenyl)dicyclohexylphosphane Sulfide (1c): Colourless oil (346 mg, 93% yield). R_f = 0.6 (pentane/Et_2O, 9:1). ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 58.8 (s, PCy_2) ppm. ^{1}H NMR ($CDCl_3$): δ = 1.23–1.54 (m, 10 H, CH_2), 1.78 (s, 3 H, CH_3), 1.83–1.95 (m, 12 H, CH_2), 1.98–2.09 (m, 2 H, CH_2), 2.27–2.38 (m, 2 H, CH_2), 4.74 (s, 1 H, C=CH_2), 4.77 (s, 1 H, C=CH_2) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 22.6 (s, 1 C, CH_3), 24.0 (d, $^1J_{CP}$ = 46 Hz, 2 C, CH_2), 25.9 (d, $^4J_{CP}$ = 1.5 Hz, 2 C, CH_2), 26.1 (d, $^3J_{CP}$ = 3 Hz, 2 C, CH_2), 26.3 (d, $^3J_{CP}$ = 3 Hz, 2 C, CH_2), 26.5 (d, $^2J_{CP}$ = 3.8 Hz, 2 C, CH_2), 26.7 (d, $^2J_{CP}$ = 3.8 Hz, 2 C, CH_2), 31.0 (d, $^3J_{CP}$ = 3 Hz, 1 C, CH_2), 38.7 (d, $^1J_{CP}$ = 47.5 Hz, 1 C, CH), 110.1 (s, 1 C, C=*C*H_2), 145.1 (d, $^4J_{CP}$ = 13.6 Hz, 1 C, *C*=CH_2) ppm. $C_{17}H_{31}PS$ (298.5): calcd. C 68.41, H 10.47, S 10.74; found C 68.42, H 10.44, S 10.69.

(7-Methyl-3-methylene-6-octenyl)diphenylphosphane Sulfide (1d): Colourless oil (416 mg, 94% yield). R_f = 0.5 (pentane/Et_2O, 9:1). ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 42.7 (s, PPh_2) ppm. ^{1}H NMR ($CDCl_3$): δ = 1.58 [s, 3 H, =C(CH_3)$_2$], 1.68 [s, 3 H, =C(CH_3)$_2$], 2.02–2.11 (m, 4 H, CH_2), 2.33 (m, 2 H, CH_2), 2.59 (m, 2 H, CH_2P), 4.79 (pseudo s, 2 H, =CH_2), 5.07 (m, 1 H, CH), 7.44–7.53 (m, 6 H, Ph), 7.82–7.90 (m, 4 H, Ph) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 17.8 [s, 1 C, =C(*C*H_3)$_2$], 25.7 [s, 1 C, =C(*C*H_3)$_2$], 26.3 (s, 1 C, CH_2), 28.4 (d, $^2J_{CP}$ = 1.6 Hz, 1 C, CH_2), 31.1 (d, $^1J_{CP}$ = 56.3 Hz, 1 C, CH_2), 36.1 (s, 1 C, CH_2), 109.52 (s, 1 C, =CH_2), 123.7 (s, 1 C, =CH), 128.7 (d, $^2J_{CP}$ = 11.8 Hz, 4 C, *o*-Ph), 131.1 (d, $^3J_{CP}$ = 10.1 Hz, 4 C, *m*-Ph), 131.5 (d, $^4J_{CP}$ = 3.0 Hz, 2 C, *p*-Ph), 131.9 [s, 1 C, =*C*(CH$_3$)$_2$], 132.7 (d, $^1J_{CP}$ = 80.1 Hz, 2 C, *ipso*-Ph), 148.40 (d, $^3J_{CP}$ = 16.7 Hz, 1 C, *C*=CH_2) ppm. $C_{22}H_{27}PS$ (354.49): calcd. C 74.54, H 7.68, S 9.05; found C 74.88, H 7.43, S 9.11.

(7-Methyl-3-methylene-6-octenyl)(methyl)phenylphosphane Sulfide (1e): Colourless oil (336 mg, 92% yield). R_f = 0.5 (pentane/Et_2O, 9:1). ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 37.8 (s, PMePh) ppm. ^{1}H NMR ($CDCl_3$): δ = 1.58 [s, 3 H, =C(CH_3)$_2$], 1.68 [s, 3 H, =C(CH_3)$_2$], 1.99 (d, $^2J_{PH}$ = 12.6 Hz, 3 H, P-CH_3), 2.03–2.06 (m, 4 H, CH_2), 2.19–2.29 (m, 4 H, CH_2), 4.74 (s, 1 H, =CH_2), 4.78 (s, 1 H, =CH_2), 5.06 (m, 1 H, C=CH), 7.40–7.60 (m, 3 H, Ph), 7.81–7.90 (m, 2 H, Ph) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 17.7 [s, 1 C, =C(*C*H_3)$_2$], 20.8 (d, $^1J_{CP}$ = 55.8 Hz, 1 C, P-CH_3), 25.6 [s, 1 C, =C(*C*H_3)$_2$], 26.1 (s, 1 C, CH_2), 33.1 (d, $^1J_{CP}$ = 53.1 Hz, 1 C, CH_2), 35.9 (s, 1 C, CH_2), 39.6 (d, $^2J_{CP}$ = 2.5 Hz, 1 C, CH_2), 109.5 (s, 1 C, =CH_2), 123.6 (s, 1 C, Me_2C=*C*H), 128.6 (d, $^2J_{CP}$ = 11.3 Hz, 2 C, *o*-Ph), 130.4 (d, $^3J_{CP}$ = 10.1 Hz, 2 C, *m*-Ph), 131.6 (d, $^4J_{CP}$ = 2.8 Hz, 1 C, *p*-Ph), 132.1 [s, 1 C, =*C*(CH$_3$)$_2$], 132.2 (d, $^1J_{CP}$ = 80.3 Hz, 1 C, *ipso*-Ph), 148.0 (d, $^3J_{CP}$ = 15.8 Hz, 1 C, =*C*CH_3) ppm. $C_{17}H_{25}PS$ (292.42): calcd. C 69.82, H 8.62, S 10.97; found C 70.07, H 8.50, S 10.86.

[2-(6,6-Dimethylbicyclo[3.1.1]-2-heptenyl)ethyl]diphenylphosphane Sulfide (1h): Colourless oil (398 mg, 87% yield). R_f = 0.5 (pentane/Et_2O, 9:1). ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 41.1 (s, PPh_2) ppm. ^{1}H NMR ($CDCl_3$): δ = 0.53 (s, 3 H, CH_3), 1.16 (s, 3 H, CH_3), 1.21 (m, 1 H, CH_2), 1.73–1.78 (m, 2 H, CH_2), 1.92 (m, 1 H, CH_2), 2.10 (m, 1 H, CH), 2.15–2.35 (m, 2 H, CH_2), 2.61 (t, $^3J_{HH}$ = 5.4 Hz, 1 H, CH), 3.21 (td, $^2J_{PH}$ = 14.6, $^2J_{HH}$ = 7.2 Hz, 1 H, CH_2), 3.35 (td, $^2J_{PH}$ = 14.6, $^3J_{HH}$ = 8.2 Hz, 1 H, CH_2), 5.12 (pseudo q, $^3J_{HH}$ = $^3J_{PH}$ = 7.5 Hz, 1 H, =CH), 7.40–7.51 (m, 6 H, Ph), 7.75–7.92 (m, 4 H, Ph) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 19.0 (d, $^5J_{CP}$ = 2.3 Hz, 1 C, CH_2), 20.9 (s, 1 C, CH_3), 22.4 (s, 1 C, CH_2), 24.9 (s, 1 C, CH_3), 26.6 (d, $^2J_{CP}$ = 3.8 Hz, 1 C, CH_2), 32.3 (d, $^1J_{CP}$ = 54.8 Hz, 1 C, CH_2), 39.5 (d, $^5J_{CP}$ = 4.5 Hz, 1 C, CH), 39.5 [s, 1 C, *C*(CH$_3$)$_2$], 51.6 (d, $^4J_{CP}$ = 2.3 Hz, 1 C, CH), 109.3 (d, $^2J_{CP}$ = 8.3 Hz, 1 C, =CH), 127.3 (d, $^2J_{CP}$ = 12 Hz, 2 C, *o*-Ph), 127.5 (d, $^2J_{CP}$ = 11.3 Hz, 2 C, *o*-Ph), 130.1 (d, $^3J_{CP}$ = 9.8 Hz, 2 C, *m*-Ph), 130.3 (d, $^4J_{CP}$ = 3.8 Hz, 1 C, *p*-Ph), 130.4 (d, $^4J_{CP}$ = 3.8 Hz, 1 C, *p*-Ph), 130.5 (d, $^3J_{CP}$ = 9.8 Hz, 2 C, *m*-Ph), 131.5 (d, $^1J_{CP}$ = 78.8 Hz, 1 C, *ipso*-Ph), 132.3 (d, $^1J_{CP}$ = 78.8 Hz, 1 C, *ipso*-Ph), 147.5 (d, $^3J_{CP}$ = 13.5 Hz, 1 C, *C*=CH) ppm. $C_{23}H_{27}PS$ (366.50): calcd. C 75.37, H 7.43, S 8.75; found C 75.36, H 7.49, S 9.01.

(Cyclohex-3-enyl)diphenylphosphane Sulfide (1i): Colourless oil (324 mg, 87% yield). R_f = 0.5 (pentane/Et_2O, 9:1). ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 49.8 (s, PPh_2) ppm. ^{1}H NMR ($CDCl_3$): δ = 1.70–1.91 (m, 3 H, CH_2), 2.01–2.25 (m, 2 H, CH_2), 2.49 (m, 1 H, CH_2), 2.86 (m, 1 H, CH), 5.65–5.78 (m, 2 H, =CH), 7.43–7.54 (m, 6 H, Ph),

7.89–8.02 (m, 4 H, Ph) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 21.8 (d, J_{CP} = 1.5 Hz, 1 C, CH_2), 24.2 (s, 1 C, CH_2), 25.0 (d, J_{CP} = 14.3 Hz, 1 C, CH_2), 34.2 (d, $^1J_{CP}$ = 58.1 Hz, 1 C, CH), 125.6 (d, J_{CP} = 14.3 Hz, 1 C, =CH), 126.5 (d, J_{CP} = 1.5 Hz, 1 C, =CH), 128.5 (d, $^2J_{CP}$ = 11.3 Hz, 2 C, *o*-Ph), 128.6 (d, $^2J_{CP}$ = 11.3 Hz, 2 C, *o*-Ph), 130.9 (d, $^1J_{CP}$ = 77.7 Hz, 1 C, *ipso*-Ph), 131.3 (d, $^4J_{CP}$ = 4.5 Hz, 1 C, *p*-Ph), 131.4 (d, $^3J_{CP}$ = 9 Hz, 2 C, *m*-Ph), 131.4 (d, $^4J_{CP}$ = 4.5 Hz, 1 C, *p*-Ph), 131.5 (d, $^3J_{CP}$ = 9 Hz, 2 C, *m*-Ph), 131.9 (d, $^1J_{CP}$ = 77 Hz, 1 C, *ipso*-Ph) ppm. $C_{18}H_{19}PS$ (298.38): calcd. C 72.45, H 6.42, S 10.75; found C 72.69, H 6.25, S 10.84.

(2,3-Dimethyl-2-butenyl)diphenylphosphane Sulfide (2f): Colourless oil (334 mg, 89% yield). R_f = 0.6 (pentane/Et_2O, 9:1). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 39.1 (s, PPh_2) ppm. ^1H NMR ($CDCl_3$): δ = 1.35 [d, $^5J_{PH}$ = 4 Hz, 3 H, =C(CH_3)$_2$], 1.60 (m, 3 H, =CCH_3), 1.63 [d, $^5J_{PH}$ = 6.4 Hz, 3 H, =C(CH_3)$_2$], 3.45 (d, $^2J_{PH}$ = 14.1 Hz, 2 H, CH_2), 7.42–7.55 (m, 6 H, Ph), 7.84–7.92 (m, 4 H, Ph) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 20.6 (d, $^3J_{CP}$ = 1.1 Hz, 1 C, =C*C*H_3), 20.9 [d, $^4J_{CP}$ = 3.3 Hz, 1 C, =C(*C*H_3)$_2$], 21.2 [d, $^4J_{CP}$ = 3.3 Hz, 1 C, =C(*C*H_3)$_2$], 40.2 (d, $^1J_{CP}$ = 52.2 Hz, 1 C, CH_2), 118.4 (d, $^2J_{CP}$ = 10.4 Hz, 1 C, =*C*CH_3), 128.4 (d, $^2J_{CP}$ = 11.7 Hz, 4 C, *o*-Ph), 131.3 (d, $^4J_{CP}$ = 2.7 Hz, 2 C, *p*-Ph), 131.4 [d, $^3J_{CP}$ = 12.1 Hz, 1 C, =*C*(CH_3)$_2$], 131.5 (d, $^3J_{CP}$ = 9.7 Hz, 4 C, *m*-Ph), 133.4 (d, $^1J_{CP}$ = 77.4 Hz, 2 C, *ipso*-Ph) ppm. $C_{18}H_{21}PS$ (300.4): calcd. C 71.97, H 7.05, S 10.67; found C 71.95, H 7.26, S 10.93.

(2,3-Dimethyl-2-butenyl)(methyl)phenylphosphane Sulfide (2g): Colourless oil (268 mg, 90% yield). R_f = 0.6 (pentane/Et_2O, 9:1). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 36.1 (s, PMePh) ppm. ^1H NMR ($CDCl_3$): δ = 1.46 [d, $^5J_{PH}$ = 3.4 Hz, 3 H, =C(CH_3)$_2$], 1.64 (m, 3 H, =CCH_3), 1.66 [d, $^5J_{PH}$ = 5.2 Hz, 3 H, =C(CH_3)$_2$], 2.0 (d, $^2J_{PH}$ = 12.8 Hz, 3 H, PCH_3), 2.98 (pseudo t, $^2J_{PH}$ = $^2J_{HH}$ = 14.8 Hz, 1 H, CH_2), 3.09 (pseudo t, $^2J_{PH}$ = $^2J_{HH}$ = 14.5 Hz, 1 H, CH_2), 7.40–7.60 (m, 3 H, Ph), 7.80–7.92 (m, 2 H, Ph) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 20.1 (d, $^1J_{CP}$ = 55.8 Hz, 1 C, P-CH_3), 20.7 (d, $^3J_{CP}$ = 1.4 Hz, 1 C, =C*C*H_3), 20.8 [d, $^4J_{CP}$ = 3.6 Hz, 1 C, =C(*C*H_3)$_2$], 21.3 [d, $^4J_{CP}$ = 3.5 Hz, 1 C, =C(*C*H_3)$_2$], 43.5 (d, $^1J_{CP}$ = 50.1 Hz, 1 C, CH_2), 119.2 (d, $^2J_{CP}$ = 11.2 Hz, 1 C, =*C*CH_3), 128.4 (d, $^2J_{CP}$ = 11.7 Hz, 2 C, *o*-Ph), 130.7 (d, $^3J_{CP}$ = 9.9 Hz, 2 C, *m*-Ph), 130.8 [d, $^3J_{CP}$ = 11.8 Hz, 1 C, =*C*(CH_3)$_2$], 131.4 (d, $^4J_{CP}$ = 3.0 Hz, 1 C, *p*-Ph), 133.2 (d, $^1J_{CP}$ = 75.1 Hz, 1 C, *ipso*-Ph) ppm. $C_{13}H_{19}PS$ (238.3): calcd. C 65.51, H 8.04, S 13.45; found C 65.56, H 7.95, S 13.69.

(2-Phenylethyl)diphenylphosphane Sulfide (3): White solid (358 mg, 89% yield, m.p. 94 °C). R_f = 0.6 (pentane/Et_2O, 9:1). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 41.9 (s, PPh_2) ppm. ^1H NMR ($CDCl_3$): δ = 2.72–2.84 (m, 2 H, CH_2), 2.80–3.10 (m, 2 H, CH_2), 7.16–7.24 (m, 3 H, Ph), 7.25–7.32 (m, 2 H, Ph), 7.44–7.56 (m, 6 H, Ph), 7.84–7.92 (m, 4 H, Ph) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 28.4 (d, $^2J_{CP}$ = 1.7 Hz, 1 C, CH_2), 34.6 (d, $^1J_{CP}$ = 55.0 Hz, 1 C, CH_2), 126.4 (s, 2 C, *o*-Ph), 128.2 (s, 2 C, *m*-Ph), 128.6 (s, 1 C, *p*-Ph), 128.7 (d, $^2J_{CP}$ = 12.3 Hz, 4 C, *o*-Ph), 128.77 (s, 1 C, *ipso*-Ph), 131.1 (d, $^3J_{CP}$ = 10.2 Hz, 4 C, *m*-Ph), 131.5 (d, $^4J_{CP}$ = 2.7 Hz, 2 C, *p*-Ph), 132.6 (d, $^1J_{CP}$ = 80.0 Hz, 2 C, *ipso*-Ph) ppm. $C_{20}H_{19}PS$ (322.4): calcd. C 74.51, H 5.94, S 9.95; found C 74.82, H 6.11, S 10.17.

(2-Phenylethyl)dicyclohexylphosphane Sulfide (4): Colourless oil (283 mg, 75% yield). R_f = 0.5 (pentane/Et_2O, 9:1). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 58.4 (s, PCy_2) ppm. ^1H NMR ($CDCl_3$): δ = 1.17–1.46 (m, 10 H, CH_2), 1.74–1.87 (m, 12 H, CH_2), 1.93–1.97 (m, 2 H, CH_2), 2.97–3.01 (m, 2 H, CH_2), 7.19–7.26 (m, 3 H, Ph), 7.30–7.37 (m, 2 H, Ph) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 25.9 (d, $^4J_{CP}$ = 1.5 Hz, 2 C, CH_2), 26.2 (d, $^3J_{CP}$ = 3 Hz, 2 C, CH_2), 26.4 (d, $^3J_{CP}$ = 3 Hz, 2 C, CH_2), 26.6 (d, $^2J_{CP}$ = 3.8 Hz, 2 C, CH_2), 26.7 (d, $^2J_{CP}$ = 3.8 Hz, 2 C, CH_2), 27.7 (d, $^1J_{CP}$ = 44.5 Hz, 2 C, CH_2), 29.5 (d, $^2J_{CP}$ = 3 Hz, 1 C, CH_2), 37.8 (d, $^1J_{CP}$ = 47.5 Hz, 1 C, CH), 126.4 (s, 1 C, *p*-Ph), 128.2 (s, 2 C, *o*-Ph), 128.7 (s, 2 C, *m*-Ph), 141.5 (s, 1 C, *ipso*-Ph) ppm.

(2,2-Diphenylethyl)diphenylphosphane Sulfide (5): White solid (418 mg, 84% yield). R_f = 0.6 (pentane/Et_2O, 9:1). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 41.8 (s, PPh_2) ppm. ^1H NMR ($CDCl_3$): δ = 3.18 (dd, $^2J_{PH}$ = 11.4, $^3J_{HH}$ = 6.9 Hz, 2 H, CH_2), 4.86 (dt, $^3J_{PH}$ = 14.1, $^3J_{HH}$ = 6.9 Hz, 1 H, CH), 7.01–7.88 (m, 20 H, Ph) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 38.6 (d, $^1J_{CP}$ = 55.8 Hz, 1 C, CH_2), 45.1 (s, 1 C, CH), 126.4 (s, 2 C, *p*-Ph), 128.0 (s, 4 C, *o*-Ph), 128.2 (d, $^2J_{CP}$ = 12.8 Hz, 4 C, *o*-Ph), 128.3 (s, 4 C, *m*-Ph), 131.0 (d, $^4J_{CP}$ = 3 Hz, 2 C, *p*-Ph), 131.1 (d, $^3J_{CP}$ = 10.5 Hz, 4 C, *m*-Ph), 132.8 (d, $^1J_{CP}$ = 80.8 Hz, 2 C, *ipso*-Ph), 143.5 (d, $^3J_{CP}$ = 8 Hz, 2 C, *ipso*-Ph) ppm. $C_{26}H_{23}PS$ (398.5): calcd. C 78.36, H 5.82, S 8.05; found C 79.01, H 5.70, S 8.38.

(1-Methyl-1-phenylethyl)diphenylphosphane Sulfide (6): Colourless oil (382 mg, 91% yield). R_f = 0.6 (pentane/Et_2O, 9:1). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 55.5 (s, PPh_2) ppm. ^1H NMR ($CDCl_3$): δ = 1.91 (s, 6 H, CH_3), 7.01–7.14 (m, 3 H, Ph), 7.27–7.39 (m, 8 H, Ph), 7.78–7.88 (m, 4 H, Ph) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 30.9 (s, 1 C, CH_3), 31.0 (s, 1 C, CH_3), 76.9 [d, $^1J_{CP}$ = 47.5 Hz, 1 C, *C*(CH_3)$_2$], 126.4 (s, 2 C, *o*-Ph), 127.2 (s, 1 C, *p*-Ph), 128.1 (d, $^2J_{CP}$ = 14.3 Hz, 4 C, *o*-Ph), 128.4 (s, 2 C, *m*-Ph), 131.4 (d, $^4J_{CP}$ = 3 Hz, 2 C, *p*-Ph), 131.6 (d, $^3J_{CP}$ = 11.3 Hz, 4 C, *m*-Ph), 134.4 (s, 1 C, *ipso*-Ph), 134.9 (d, $^1J_{CP}$ = 80.8 Hz, 2 C, *ipso*-Ph) ppm. $C_{21}H_{21}PS$ (336.4): calcd. C 74.97, H 6.29, S 9.53; found C 75.12, H 6.29, S 9.85.

Styryldiphenylphosphane Sulfide (7): White solid (380 mg, 95% yield, *Z*/*E*: 60:40). R_f = 0.6 (pentane/Et_2O, 9:1). $C_{20}H_{17}PS$ (320.4): calcd. C 74.98, H 5.35, S 10.01; found C 74.95, H 5.35, S 10.44. (*Z*) isomer: $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 30.3 (s, PPh_2) ppm. ^1H NMR ($CDCl_3$): δ = 6.25 (dd, $^2J_{PH}$ = 17.4, $^3J_{HH}$ = 13 Hz, 1 H, =CH), 6.85–6.95 (m, 3 H, Ph), 7.13–7.20 (m, 6 H, Ph), 7.25 (d, $^3J_{HH}$ = 13 Hz, 1 H, =CH), 7.33–7.36 (m, 2 H, Ph), 7.70–7.75 (m, 4 H, Ph) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 123.1 (d, $^1J_{CP}$ = 81.4 Hz, 1 C, =CH), 127.6 (s, 2 C, Ph), 128.4 (d, $^2J_{CP}$ = 12 Hz, 4 C, *o*-Ph), 128.9 (d, $^4J_{CP}$ = 2.3 Hz, 2 C, *p*-Ph), 130.3 (s, 2 C, Ph), 131.2 (d, $^3J_{CP}$ = 10.5 Hz, 4 C, *m*-Ph), 131.3 (s, 1 C, Ph), 133.1 (d, $^1J_{CP}$ = 85 Hz, 2 C, *ipso*-Ph), 134.5 (d, $^3J_{CP}$ = 6.8 Hz, 1 C, *ipso*-Ph), 146.6 (d, $^2J_{CP}$ = 2.3 Hz, 1 C, =CH) ppm. (*E*) isomer: $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 37.2 (s, PPh_2) ppm. ^1H NMR ($CDCl_3$): δ = (d, 1 H, =CH), 6.85–6.95 (m, 3 H, Ph), 7.15–7.25 (m, 6 H, Ph), 7.33–7.36 (m, 2 H, Ph), 7.51 (dd, J_{PH} = 22.2, $^3J_{HH}$ = 16.3 Hz, 1 H, =CH), 7.70–7.75 (m, 4 H, Ph) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 119.9 (d, $^1J_{CP}$ = 86.7 Hz, 1 C, =CH), 127.9 (s, 1 C, *p*-Ph), 128.8 (d, $^2J_{CP}$ = 12 Hz, 4 C, *o*-Ph), 130.2 (d, $^4J_{CP}$ = 5.3 Hz, 2 C, *o*-Ph), 131.3 (s, 2 C, *m*-Ph), 131.5 (d, $^3J_{CP}$ = 10.5 Hz, 4 C, *m*-Ph), 131.6 (d, $^4J_{CP}$ = 3 Hz, 2 C, *p*-Ph), 133.1 (d, $^1J_{CP}$ = 85 Hz, 2 C, *ipso*-Ph), 135.0 (d, $^3J_{CP}$ = 19.6 Hz, 1 C, *ipso*-Ph), 147.9 (d, $^2J_{CP}$ = 6 Hz, 1 C, =CH) ppm.

(1,2-Diphenylvinyl)diphenylphosphane Sulfide (8): White solid (460 mg, 93% yield, *Z*/*E*: 60:40). R_f = 0.6 (pentane/Et_2O, 9:1). $C_{26}H_{21}PS$ (396.5): calcd. C 78.76, H 5.34, S 8.09; found C 79.02, H 5.29, S 8.27. (*Z*) isomer: $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 36.3 (s, PPh_2) ppm. ^1H NMR ($CDCl_3$): δ = 6.80–6.85 (m, 2 H, Ph), 6.91–6.94 (m, 2 H, Ph), 7.03–7.24 (m, 6 H, Ph), 7.39–7.55 (m, 6 H, Ph), 7.67 (d, $^3J_{PH}$ = 26 Hz, 1 H, =CH), 7.75–7.85 (m, 4 H, Ph) ppm. (*E*) isomer: $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 48.05 (s, PPh_2) ppm. ^1H NMR ($CDCl_3$): δ = 6.97–7.05 (m, 2 H, Ph), 7.09–7.25 (m, 8 H, Ph), 7.28 (s, 1 H, =CH), 7.35–7.45 (m, 2 H, Ph), 7.53–7.67 (m, 4 H, Ph), 7.76–7.83 (m, 4 H, Ph) ppm.

(3,5-Cycloheptadienyl)diphenylphosphane Sulfide (9): Colorless oil (353 mg, 91% yield). R_f = 0.6 (pentane/Et_2O, 9:1). $^{31}P\{^1H\}$ NMR

Table 3. Crystal and structure refinement data for **1a**, **7** and **9**.

Compounds	**1a**	**7**	**9**
Empirical formula	$C_{17}H_{19}PS$	$C_{20}H_{17}PS$	$C_{19}H_{19}P$
Formula weight	286.36	320.38	278.31
Temperature [K]	115(2)	115(2)	115(2)
Crystal system	triclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$
a [Å]	9.2124(3)	14.7081(4)	10.1117(5)
b [Å]	9.3719(2)	6.5173(2)	9.8388(6)
c [Å]	10.0851(3)	17.5033(6)	15.1645(8)
α [°]	64.156(1)		
β [°]	89.701(1)	97.152(1)	91.134(3)
γ [°]	87.191(2)		
Volume [Å^3]	782.57(4)	1664.76(9)	1508.38(14)
Z	2	4	4
$\rho_{calcd.}$ [g/cm^3]	1.215	1.278	1.226
μ [mm^{-1}]	0.29	0.28	0.17
Size [mm^3]	$0.45 \times 0.30 \times 0.20$	$0.37 \times 0.25 \times 0.10$	$0.15 \times 0.05 \times 0.02$
$F(000)$	304	672	592
λ [Å]	0.71073	0.71073	0.71073
$\sin(\theta)/\lambda_{max}$ [Å^{-1}]	0.65	0.65	0.65
Index ranges	$-11 \geq h \leq 11$	$-18 \geq h \leq 19$	$-13 \geq h \leq 13$
	$-12 \geq k \leq 12$	$-8 \geq k \leq 7$	$-12 \geq k \leq 12$
	$-13 \geq l \leq 12$	$-22 \geq l \leq 22$	$-19 \geq l \leq 19$
Reflections collected	6644	6464	6114
R_{int}	0.016	0.026	0.047
Unique ref. [$I \geq 2\sigma(I)$]	3097	3009	2615
Data/restraints/parameters	3550/0/173	3768/0/199	3414/0/181
$R(F)[F \geq 4\sigma(F)]$[a]	0.035	0.035	0.059
$wR(F^2)$ (all data)[b]	0.090	0.082	0.123
Goodness-of-fit[c] on F^2	1.05	1.03	1.13
$\Delta\rho$ [e Å^{-3}]	0.67 and –0.33	0.29 and –0.32	0.36 and –0.29

[a] $R_1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma[w(F_o^2)^2]]^{1/2}$ in which $w = 1/[\sigma^2(F_o^2 + (0.0369P)^2 + 0.4348P)]$ for **1a**, $w = 1/[\sigma^2(F_o^2 + (0.0214P)^2 + 0.8766P)]$ for **7** and $w = 1/[\sigma^2(F_o^2 + (0.0P)^2 + 2.3806P)]$ for **9** in which $P = [\text{Max}(F_o^2,0) + 2*F_c^2]/3$. [c] $S = [\Sigma w(F_o^2 - F_c^2)(n - p)]^{1/2}$ (n = number of reflections, p = number of $p$meters).

($CDCl_3$): δ = 50.9 (s, PPh_2) ppm. ^{1}H NMR ($CDCl_3$): δ = 2.29–2.45 (m, 2 H, CH_2), 2.55–2.71 (m, 2 H, CH_2), 3.35 (dtt, $^3J_{HH}$ = 10.7, $^2J_{PH}$ = 8, $^3J_{HH}$ = 2.3 Hz, 1 H, CH), 5.77–5.88 (m, 4 H, =CH), 7.40–7.55 (m, 6 H, Ph), 7.90–8.05 (m, 4 H, Ph) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 30.9 (s, 2 C, CH_2), 35.9 (d, $^1J_{CP}$ = 53 Hz, 1 C, CH), 125.7 (s, 2 C, =CH), 128.7 (d, $^2J_{CP}$ = 12 Hz, 4 C, *o*-Ph), 131.2 (d, $^3J_{CP}$ = 9.8 Hz, 4 C, *m*-Ph), 131.4 (d, $^4J_{CP}$ = 3 Hz, 2 C, *p*-Ph), 131.8 (d, $^1J_{CP}$ = 77.7 Hz, 2 C, *ipso*-Ph), 131.9 (d, $^3J_{CP}$ = 19.6 Hz, 1 C, =CH) ppm. $C_{19}H_{19}PS$ (310.39): calcd. C 73.52, H 6.17, S 10.33; found C 73.45, H 6.38, S 10.57.

X-ray Analysis of Compounds 1a, 7 and 9: Intensity data were collected at 115 K with a Nonius–Kappa instrument with an APEX II detector. The structures were solved by direct methods (SIR92)[17] and refined by full-matrix least-squares methods based on F_2 (SHELXL-97)[18] with the aid of the WINGX program.[19] All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in their calculated positions and refined with a riding model. The crystallographic data are reported in Table 3.

CCDC-739865 (for **1a**), -739864 (for **7**) and -739866 (for **9**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

This work was supported by the Agence Nationale de la Recherche (ANR MetChirPhos).

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Received: December 3, 2009
Published Online: January 29, 2010

