Scope and Limitations of the Peterson Olefination Reaction as a Route to Vinylidene Phosphanes

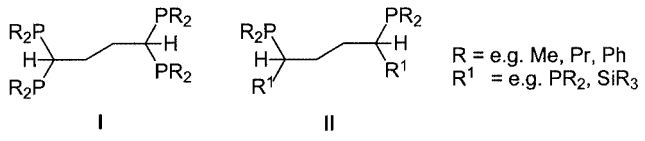
Keith Izod,*[a] William McFarlane,[a] and Brent V. Tyson[a]

Keywords: Olefination / Phosphorus / Peterson / Protecting groups

The Peterson olefination reaction has been investigated as a route to novel P-substituted alkenes. The reaction between $[(n\mathrm{Pr_2P})_2(\mathrm{Me_3Si})\mathrm{C}]\mathrm{Li}$ and paraformaldehyde cleanly gives the symmetrical vinylidene phosphane $(n\mathrm{Pr_2P})_2\mathrm{C{=}CH_2}$ (**4**) in good to excellent yields. In contrast, reactions between $[(\mathrm{R_2P})(\mathrm{Me_3Si})_2\mathrm{C}]\mathrm{Li}$ (R = Me, *n*Pr) and paraformaldehyde yield complex mixtures of products which do not contain the expected vinylidene species. However, the unsymmetrical vinylidene phosphanes $[n\mathrm{Pr_2P(BH_3)}](\mathrm{Me_3Si})\mathrm{C{=}CH_2}$ (**6**), $(\mathrm{Ph_2P})(i\mathrm{Pr_2P})\mathrm{C{=}CH_2}$ (**7**), $[n\mathrm{Pr_2P(S)}](\mathrm{Me_3Si})\mathrm{C{=}CH_2}$ (**10**), $[\mathrm{Ph_2P(S)}][i\mathrm{Pr_2P(S)}]\mathrm{C{=}CH_2}$ (**11**) and $[\mathrm{Ph_2P(S)}][\mathrm{Me_2P(S)}]\mathrm{C{=}CH_2}$ (**12**) are readily accessible by the Peterson olefination reaction {compound **7** is obtained by deprotection of the corresponding borane adduct $[\mathrm{Ph_2P(BH_3)}][i\mathrm{Pr_2P(BH_3)}]\mathrm{C{=}CH_2}$ with pyrrolidine}.

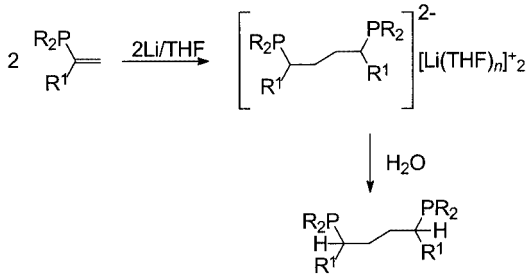
Introduction

Polyphosphanes such as the tripodal triphosphane $\mathrm{MeC(CH_2PPh_2)_3}$ are excellent ligands for the stabilization of low oxidation state transition metal complexes, many of which act as (pre-)catalysts for important organic transformations;[1] for example, the bimetallic complex *rac*-$[\{[\mathrm{Et_2PCH_2CH_2P(Ph)}]_2\mathrm{CH_2}\}\mathrm{Rh_2(norbornadiene)_2}][\mathrm{BF_4}]_2$ is a highly efficient pre-catalyst for the regioselective hydroformylation of α-olefins.[2] Diphosphanes in which the two phosphorus atoms are separated by a single carbon such as $(\mathrm{Ph_2P})_2\mathrm{CH_2}$ (dppm) and $(\mathrm{Me_2P})_2\mathrm{CH_2}$ (dmpm) are also of enormous value and form a particularly useful sub-class of "A-frame" ligands which are able to support bi- and polynuclear transition metal complexes.[3]



I II

We have recently become interested in the synthesis of new polyphosphane ligands **I** and **II**, the former of which incorporate the P−C−P unit found in dppm and dmpm. These new ligands are prepared by a Schlenk dimerization protocol from vinylidene phosphanes of the form $(\mathrm{R_2P})\mathrm{R^1C{=}CH_2}$ ($\mathrm{R^1}$ = e.g. $\mathrm{R_2P}$, $\mathrm{R^2_2P}$, $\mathrm{Me_3Si}$), according to Scheme 1.[4]



Scheme 1

Although we have successfully employed this methodology for the synthesis of a range of new polyphosphanes, this reaction potentially suffers from the drawback that there have, until now, been few readily available vinylidene phosphane precursors. When we began this work only the diphosphanes $(\mathrm{Ph_2P})_2\mathrm{C{=}CHR}$ [R = H (**1a**), Ph (**1b**)] and the corresponding disulfides $[\mathrm{Ph_2P(S)}]_2\mathrm{C{=}CHR}$ [R = H (**2a**), Ph (**2b**)] had been reported. The diphosphane **1a** may be prepared in moderate yield from the reaction between $\mathrm{Ph_2PLi}$ and vinylidene chloride (Scheme 2).[5]

$$2\ \mathrm{Ph_2PLi} + \mathrm{Cl_2C{=}CH_2} \longrightarrow (\mathrm{Ph_2P})_2\mathrm{C{=}CH_2}\ (\mathbf{1a}) + 2\ \mathrm{LiCl}$$

Scheme 2

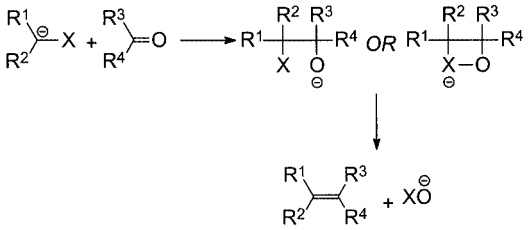
This reaction is suitable only for the synthesis of symmetrical vinylidene phosphanes and is limited to examples where the lithium phosphanide precursor is readily accessible. In our hands this reaction has failed to give significant quantities of vinylidene phosphanes with substituents other

[a] Chemistry, School of Natural Sciences, University of Newcastle, Newcastle upon Tyne, NE1 7RU, UK
Fax: (internat.) + 44-(0)191-222-6929
E-mail: k.j.izod@ncl.ac.uk

than phenyl at the phosphorus center, most likely due to the ready anionic polymerization of vinylidene species. For example, the reaction between two equivalents of Cy_2PLi and vinylidene chloride under the same conditions employed in the synthesis of $(Ph_2P)_2C{=}CH_2$ gave only an intractable sticky solid which was free of the desired vinylidene phosphane $(Cy_2P)_2C{=}CH_2$ (Cy = cyclohexyl).

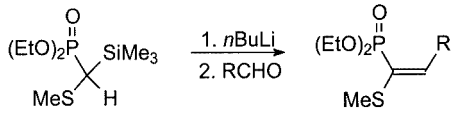
Grim and Goli have reported the synthesis of **2a** and **2b** by the reaction of $[\{Ph_2P(S)\}_2CH]Li$ with either paraformaldehyde or benzaldehyde, respectively.[6] The corresponding diphosphanes **1** were obtained from the disulfides by treatment with Si_2Cl_6. We have found that, where the substituents at phosphorus are other than phenyl, similar reactions between phosphane-substituted organolithiums and paraformaldehyde do not yield the corresponding vinylidene phosphanes.

In order to increase the range and availability of vinylidene phosphanes we have initiated a study into their synthesis by a relatively straightforward Peterson olefination protocol. The Peterson olefination reaction is one of a group of several olefination protocols dependent on the elimination of a heteroatom-containing leaving group from a heteroatom-stabilized "carbanion", which includes Wittig, Horner−Wittig, Horner−Wadsworth−Emmons (HWE) and Julia olefinations (Scheme 3).[7]



Scheme 3

It has been demonstrated, that in substrates where competitive Peterson and Horner−Wittig/HWE or Julia eliminations may take place, it is the Peterson reaction which dominates.[8,9] For example, the reaction of $[\{(EtO)_2P(O)\}(MeS)(Me_3Si)C]Li$ with aldehydes gives the Peterson olefination product as the (*E*)-isomer in good yields (Scheme 4).[9] However, although the Peterson olefination reaction is an excellent method for the synthesis of variously substituted alkenes, this methodology has been applied to the synthesis of phosphorus(III)-substituted alkenes to only a limited extent. This is in spite of the fact that Peterson himself reported the syntheses of the vinylphosphanes $Ph_2PCH{=}CR^1R^2$ [R^1 = Ph; R^2 = H, Ph] and the vinylphosphane sulfide $Ph_2P(S)CH{=}CPh_2$ in moderate yields in his original paper on silyl-based olefinations in 1968.[10]



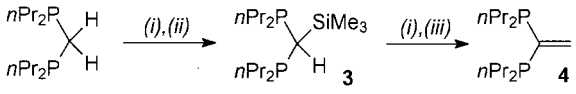
Scheme 4

The Peterson olefination of P^V-substituted carbanions is more established:[9] Savignac and co-workers have used the Peterson reaction for the synthesis of α-fluorovinylphosphonates,[11] whereas Collignon and co-workers have used this reaction for the synthesis of phosphonate-substituted penta-1,3-dienes.[12]

We now report the use of a relatively straightforward Peterson olefination protocol for the synthesis of a range of vinylidene phosphanes and vinylidene phosphane sulfides.

Results and Discussion

Treatment of the symmetrical diphosphane $(n\mathrm{Pr}_2P)_2CH_2$ with one equivalent of *t*BuLi, followed by one equivalent of Me_3SiCl yields the corresponding α-silyl-substituted diphosphane $(n\mathrm{Pr}_2P)_2(Me_3Si)CH$ (**3**) (Scheme 5). Reaction of **3** with one equivalent of *t*BuLi, followed by an excess of paraformaldehyde gives, after a simple aqueous workup, the corresponding vinylidene phosphane $(n\mathrm{Pr}_2P)_2C{=}CH_2$ (**4**) in good yield (Table 1). Compound **4** is isolated as a colorless, volatile oil, which may be purified by distillation under reduced pressure.

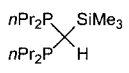
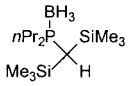
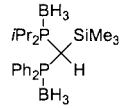
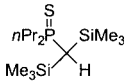
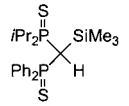
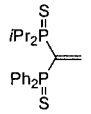
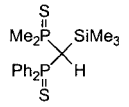
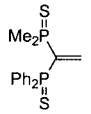


Scheme 5. (i) *t*BuLi, light petroleum 16 h; (ii) Me_3SiCl, −78 °C 2 h; (iii) CH_2O 1 h, then H_2O

Attempts to prepare the corresponding vinylidene phosphanes $(R_2P)_2C{=}CH_2$ [R = Cy or *i*Pr] by this method failed; after an aqueous workup we were able to recover only the silyl-substituted starting materials $(R_2P)_2(Me_3Si)$-CH (R = Cy, *i*Pr) from these reactions. We attribute this failure to the steric demands of the substituents at phosphorus, which are likely to hinder nucleophilic attack by the sterically crowded carbanion center at the carbonyl functionality.

In contrast to the facile formation of **4**, attempts to prepare the unsymmetrical vinylidene phosphanes $(R_2P)(Me_3Si)C{=}CH_2$ [R = Me, *n*Pr] by Peterson olefination of the corresponding bis(silyl)-stabilized carbanions $(R_2P)(Me_3Si)_2C^-$ were unsuccessful. Treatment of $[(R_2P)(Me_3Si)_2C]Li$ with paraformaldehyde in THF or light petroleum at room temperature, followed by an aqueous workup with de-gassed water and removal of solvent in vacuo, gave a colorless oil containing a complex mixture of products (Scheme 6). A ^1H NMR spectrum of the crude product mixture (R = *n*Pr) indicated the presence of a small

Table 1. Isolated vinylidene phosphanes

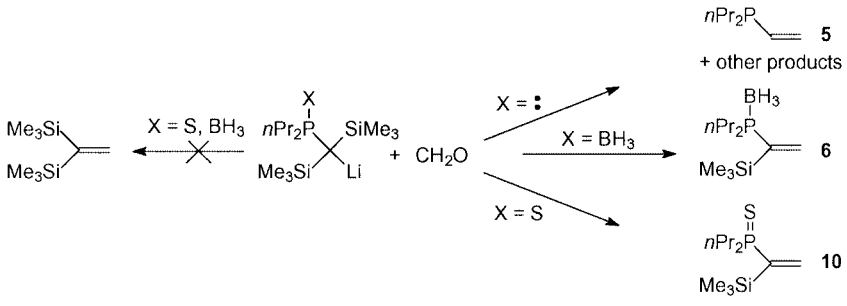
Precursor	Product	Yield (%)
 **3**	 **4**	80
 **6**	 **6**	75
 **7**	 **7**	72
 **10**	 **10**	65
 **11**	 **11**	53
 **12**	 **12**	40

amount of unchanged starting material, $(n\mathrm{Pr_2P})(\mathrm{Me_3Si})_2$-CH, along with other species containing $n\mathrm{Pr_2P}$, $\mathrm{SiMe_3}$ and vinyl fragments. The $^{31}P\{^1H\}$ NMR spectrum of this mixture contains numerous peaks, with major signals at −43.2, −28.8 and −28.0 ppm. There is no evidence for the expected vinylidene phosphane $(n\mathrm{Pr_2P})(\mathrm{Me_3Si})C{=}CH_2$ or for species containing P^V. Flash distillation of the crude reaction mixture under reduced pressure (20 °C, 0.1 Torr) gave a colorless oil which was identified as the vinylphosphane $n\mathrm{Pr_2PCH{=}CH_2}$ (**5**). Analysis of the crude reaction mixture, after treatment with elemental sulfur, by GC-MS indicates that **5** is formed in approximately 57% yield in this reaction, along with about 20 further products. At lower temperatures this reaction fails to proceed at all: when the reaction between $[(n\mathrm{Pr_2P})(\mathrm{Me_3Si})_2C]Li$ and paraformaldehyde was carried out at either −20 or −78 °C only the starting material $(n\mathrm{Pr_2P})(\mathrm{Me_3Si})_2CH$ was recovered.

The isolation of the vinylphosphane **5** from this reaction is somewhat unexpected, especially in light of the facile formation of **4** and the previously reported high yield synthesis of the vinylidene silane $(\mathrm{Me_3Si})_2C{=}CH_2$ by the Peterson olefination of $(\mathrm{Me_3Si})_3CLi$ with paraformaldehyde.[13] In this regard, it is interesting to note that Grim and Goli report that the reaction between $[\{\mathrm{Ph_2P(S)}\}_2CH]K$ and paraformaldehyde gives the vinylphosphane sulfide $[\mathrm{Ph_2P(S)}]CH{=}CH_2$ rather than the expected vinylidene species.[6]

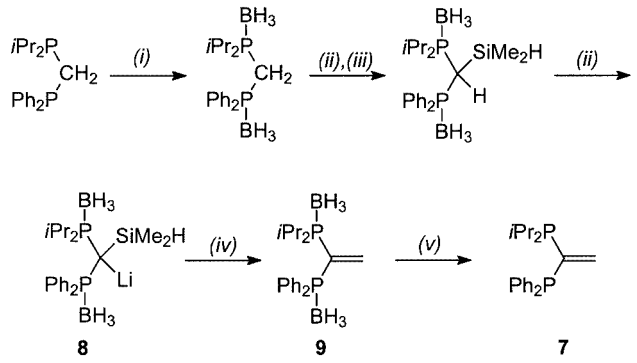
Whereas attempts to prepare $(n\mathrm{Pr_2P})(\mathrm{Me_3Si})C{=}CH_2$ by a Peterson olefination protocol failed, the reaction between the corresponding phosphane-borane derivative $[\{n\mathrm{Pr_2P(BH_3)}\}(\mathrm{Me_3Si})_2C]Li$ and paraformaldehyde gave the borane-protected vinylidene phosphane $[n\mathrm{Pr_2P(BH_3)}]$-$(\mathrm{Me_3Si})C{=}CH_2$ (**6**) in high yield (Scheme 6). Unfortunately, due to the strongly basic nature of the phosphane moiety, attempts to remove the borane protecting group from this compound using either Et_2NH or pyrrolidine were unsuccessful. It has been reported previously that α-lithiated phosphane-borane complexes behave similarly to α-lithiated phosphane oxides and undergo Horner-type elimination on treatment with aldehydes to give the corresponding alkenes.[14] The reaction between $[\{n\mathrm{Pr_2P(BH_3)}\}(\mathrm{Me_3Si})_2C]Li$ and paraformaldehyde may, therefore, proceed by either a Peterson or a Horner−Wittig-type olefination pathway to give a phosphane-substituted or a silyl-substituted alkene, respectively (Scheme 6). However, we see no evidence for the Horner−Wittig product in this reaction, consistent with previous observations on substrates where competitive Horner and Peterson olefinations may take place.[9]

The unsymmetrical vinylidene bis(phosphane) $(\mathrm{Ph_2P})$-$(i\mathrm{Pr_2P})C{=}CH_2$ (**7**) is accessible by the Peterson olefination of in situ-generated $[\mathrm{Ph_2P(BH_3)}][i\mathrm{Pr_2P(BH_3)}](\mathrm{Me_2HSi})$-C]Li (**8**) with paraformaldehyde and subsequent deprotec-



Scheme 6

tion of the adduct $[Ph_2P(BH_3)][iPr_2P(BH_3)]C{=}CH_2$ (**9**) with pyrrolidine (Scheme 7). We find that the use of the less sterically demanding dimethylsilyl substituent in the organolithium compound gives greater yields of **7** and that simply stirring the borane adduct with pyrrolidine for 12 h results in deprotection of both phosphane functionalities. We attribute the ease with which the borane protecting group may be removed in this case to the steric bulk of the phosphane substituents.



Scheme 7. (i) 2 BH_3SMe_2, diethyl ether, 1 h; (ii) *n*BuLi, THF, 12 h; (iii) Me_2HSiCl, diethyl ether/THF, −78 °C; (iv) CH_2O, 1 h, then H_2O; (v) pyrrolidine, 16 h, 20 °C

In spite of the apparent problems associated with the synthesis of unsymmetrical vinylidene phosphanes, the Peterson olefination methodology may readily be employed for the synthesis of P^V-substituted alkenes.[9,11,12,15] The phosphane sulfide derivative $[\{nPr_2P(S)\}(Me_3Si)_2C]Li$ reacts rapidly with paraformaldehyde to give the corresponding vinylidene compound $[nPr_2P(S)](Me_3Si)C{=}CH_2$ (**10**) in good yield (Scheme 6). Similarly, the related compounds $[Ph_2P(S)][iPr_2P(S)]C{=}CH_2$ (**11**) and $[Ph_2P(S)][Me_2P(S)]C{=}CH_2$ (**12**) may be synthesized by this methodology (Table 1). Once again, there is no evidence for the Horner−Wittig olefination products in these reactions.

In summary, we have found that the Peterson olefination of phosphorus-substituted organolithiums proceeds cleanly to give symmetrically substituted vinylidene phosphanes, but that this reaction is more complicated for unsymmetrical systems. Unsymmetrical phosphorus-substituted alkenes are accessible when the phosphorus substituent is in the higher P^V oxidation state or when the P^{III} center is borane-protected.

Experimental Section

General Remarks: All manipulations were carried out using standard Schlenk techniques under dry nitrogen. Light petroleum (b.p. 40−60 °C), diethyl ether and THF were distilled from sodium, potassium or sodium/potassium alloy and were stored over a potassium film (with the exception of THF, which was stored over activated 4-Å molecular sieves). Dichloromethane was distilled from CaH_2 and was stored over activated 4-Å molecular sieves. Deuterated chloroform was distilled from CaH_2, deoxygenated by three freeze-pump-thaw cycles and stored over activated 4-Å molecular sieves. Organolithiums were obtained from Aldrich, *n*BuLi as a 2.5 M solution in hexanes, *t*BuLi as a 1.7 M solution in pentane; *n*PrMgCl was obtained from Aldrich as a 2.0 M solution in diethyl ether. The adduct Me_2SBH_3 was obtained as a 2.0 M solution in diethyl ether. Potassium *tert*-butoxide was purchased from Lancaster and heated under vacuum at 100 °C (10^{-3} Torr) for 4 h prior to use. Paraformaldehyde was heated under vacuum at 100 °C (10^{-3} Torr) prior to use. The compounds $(Me_3Si)_2CHPCl_2$ [14] and $CH_2(PCl_2)_2$ [15] were prepared by previously published procedures. All other compounds were used as supplied.

^1H and ^{13}C NMR spectra were recorded with a Bruker AC200 or a JEOL Lambda500 spectrometer operating at 200.1, 500.1, 50.3 and 125.6 MHz, respectively. ^{31}P NMR spectra were recorded with a Bruker WM300 spectrometer operating at 121.5 MHz. ^1H and ^{13}C chemical shifts are quoted in ppm relative to tetramethylsilane and ^{31}P chemical shifts are quoted relative to external 85% H_3PO_4. Elemental analyses were obtained by the microanalysis service at London Metropolitan University, UK.

Preparation of $(nPr_2P)_2CH_2$: To a cold (−78 °C) solution of $CH_2(PCl_2)_2$ (10.54 g, 48.40 mmol) in diethyl ether (100 mL) was added *n*PrMgCl (96.80 mL, 0.193 mol), dropwise. The solution was allowed to attain room temperature and was stirred for 12 h. Deoxygenated water (3 × 50 mL) was added and the organic layer was dried with activated 4-Å molecular sieves. Solvent was removed in vacuo to give the diphosphane $(nPr_2P)_2CH_2$. Isolated yield 9.70 g, 81%. ^1H NMR ($CDCl_3$, 25 °C): δ = 0.92−1.49 (m, 28 H, Pr), 2.28 (s, 2 H, PCH_2P) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ = 16.00 (Pr), 19.23 (Pr), 25.37 (PCH_2P), 31.16 (Pr) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ = −35.6 ppm.

Preparation of $(nPr_2P)_2C{=}CH_2$ (4): To a solution of the diphosphane $(nPr_2P)_2CH_2$ (6.06 g, 24.50 mmol) in light petroleum (20 mL) was added *t*BuLi (14.41 mL, 24.50 mmol) and this solution was stirred overnight. The resulting white slurry was added dropwise to chlorotrimethylsilane (3.11 mL, 24.50 mmol) at −78 °C and allowed to stir for 2 h. The resulting solution was filtered and the filtrate was treated with *t*BuLi (14.41 mL, 24.50 mmol) and stirred for 12 h before being treated with a large excess of paraformaldehyde (4.41 g, 0.147 mol) and stirred for 1 hour. The reaction was quenched with deoxygenated water (30 mL) and the organic layer was extracted into diethyl ether (3 × 20 mL) and dried with activated 4-Å molecular sieves. Solvent was removed in vacuo yielding **4** as a colorless, air sensitive oil. Isolated yield 5.12 g, 80%. $C_{14}H_{30}P_2$ (260.3): calcd. C 64.59, H 11.62; found C 64.69, H 11.52. ^1H NMR ($CDCl_3$, 25 °C): δ = 0.80−1.68 (m, 28 H, Pr), 5.83 (t, $^3J_{PHcis} + {}^3J_{PHtrans}$ = 30 Hz, 2 H, $=CH_2$) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ = 15.90 (t, $J_{P,C}$ = 6 Hz, Pr), 19.20 (t, $J_{P,C}$ = 7 Hz, Pr), 28.76 (t, $J_{P,C}$ = 3 Hz, Pr), 149.47 (t, $J_{P,C}$ = 37 Hz, $=CH_2$) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ = −23.1 ppm.

Preparation of $[nPr_2P(BH_3)](Me_3Si)C{=}CH_2$ (6): To a cold (−78 °C) solution of $(Me_3Si)_2CHPCl_2$ (13.63 g, 52.17 mmol) in diethyl ether (100 mL) was added, dropwise, a solution of *n*PrMgCl in diethyl ether (52.17 mL, 0.104 mol). The solution was allowed to attain room temperature and was stirred for 12 h. Deoxygenated water (50 mL) was added and the organic layer was dried with activated 4-Å molecular sieves. Solvent was removed in vacuo to give crude $(nPr_2P)(Me_3Si)_2CH$, which was purified by distillation at reduced pressure (80 °C, 10^{-2} Torr). This phosphane (11.79 g, 42.64 mmol) was dissolved in diethyl ether (60 mL), treated with $BH_3.SMe_2$ (21.32 mL, 42.64 mmol) and stirred for 2 h. THF (20 mL) was added followed by *n*BuLi (17.06 mL, 42.64 mmol) and

this mixture was stirred for 2 h. A large excess of paraformaldehyde (6.40 g, 0.21 mol) was added and the mixture was stirred for 1 h. The reaction was then quenched with deoxygenated water (30 mL) and the organic layer was extracted into diethyl ether (3 × 20 mL) and dried with activated 4-Å molecular sieves. Solvent was removed in vacuo to give **6** as a pale yellow oil. Isolated yield 8.97 g, 75%. $C_{11}H_{28}BPSi$ (230.2): calcd. C 57.39, H 12.26; found C 57.34, H 12.00. ^{1}H NMR ($CDCl_3$, 27 °C): δ = 0.24 (s, 9 H, $SiMe_3$), 0.98−1.70 (m, 14 H, Pr), 6.38 (dd, $J_{H,H}$ = 3, $^3J_{PH}$ = 44 Hz, 1 H, =CH_2), 6.57 (dd, $J_{H,H}$ = 3, $^3J_{PH}$ = 27 Hz,1 H, =CH_2) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 27 °C): δ = 0.00 ($SiMe_3$), 15.58 (Pr), 16.46 (Pr), 27.10 (Pr), 144.47 (=CH_2) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ = 21.9 (br) ppm.

Preparation of (Ph_2P)(*i*Pr_2P)C=CH_2 (7): To a solution of methyldiphenylphosphane (4.10 g, 20.48 mmol) in diethyl ether (30 mL) was added *n*BuLi (8.36 mL, 20.48 mmol) and this mixture was left to stir for approximately 1 h. To this orange/yellow solution was added, dropwise, a solution of *t*BuOK (2.30 g, 20.48 mmol) in diethyl ether (30 mL). The yellow precipitate was isolated by filtration and washed with diethyl ether (3 × 15 mL) and residual solvent was removed in vacuo. The solid was dissolved in THF (30 mL) and added to a cold (−78 °C) solution of chlorodiisopropylphosphane (2.92 mL, 18.38 mmol) in THF (20 mL). The solvent was removed in vacuo to give a viscous brown oil which was dissolved in light petroleum (40 mL) and washed with deoxygenated water (3 × 20 mL). The organic layer was dried with activated 4-Å molecular sieves and solvent was removed in vacuo to give the diphosphane (Ph_2P)(*i*Pr_2P)CH_2 as a colorless oil.

To a solution of the diphosphane (Ph_2P)(*i*Pr_2P)CH_2 (3.66 g, 11.57 mmol) in diethyl ether (40 mL) was added BH_3·SMe_2 (11.57 mL, 23.14 mmol) and this solution was stirred for 1 h. THF (20 mL) was added, followed by *n*BuLi (5.03 mL, 11.57 mmol) and the solution was left to stir for 12 h. The deep orange solution was added dropwise to a cold (−78 °C) solution of chlorodimethylsilane (1.28 mL, 11.57 mmol) in diethyl ether (10 mL). The solution was allowed to attain room temperature and was treated with *n*BuLi (5.03 mL, 11.57 mmol) and stirred for 12 h. To the resulting solution was added paraformaldehyde (1.63 g, 54.15 mmol) and diethyl ether (20 mL), the mixture was allowed to stir for 1 hour and then deoxygenated water (30 mL) was added. The organic layer was decanted, the aqueous layer was extracted into diethyl ether (3 × 10 mL) and the combined organic extracts were dried with activated 4-Å molecular sieves. The dried solution was filtered and solvent was removed in vacuo and a small amount of light petroleum was added, yielding an off-white, crystalline solid. This solid was dissolved in pyrrolidine (8.23 g, 0.115 mol) and the solution was stirred overnight. Excess pyrrolidine was removed in vacuo and the residue was distilled under reduced pressure (oil bath temperature 150 °C, 0.01 Torr) to give **7** as a colorless oil. Isolated yield 2.85 g, 72%. ^{1}H NMR ($CDCl_3$, 25 °C): δ = 0.94 [dd, $J_{H,H}$ = 7, $^3J_{P,P}$ = 13 Hz, 6 H, $CH(CH_3)_2$], 1.03 [dd, $J_{H,H}$ = 7, $^3J_{P,P}$ = 13 Hz, 6 H, $CH(CH_3)_2$], 1.95 [m, 2 H, $CH(CH_3)_2$], 5.58 (ddd, $J_{H,H}$ = 2, $^3J_{PH}$ = 9, $^3J_{PH}$ = 19 Hz, 1 H, =CH_2), 6.06 (ddd, $J_{H,H}$ = 2, $^3J_{PH}$ = 10, $^3J_{PH}$ = 19 Hz, 1 H, =CH_2), 7.26 (m, 10 H, Ph) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ = 19.57 [$CH(CH_3)_2$], 22.82 [$CH(CH_3)_2$], 53.67 [$CH(CH_3)_2$] 128.10, 128.53, 134.13, 135.76 (Ph), 150.93 (=CH_2) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ = −4.4 (d, $J_{P,P}$ = 102 Hz, P*i*Pr_2), 15.4 (d, $J_{P,P}$ = 102 Hz, PPh_2) ppm.

Preparation of [*n*Pr_2P(S)](Me$_3$Si)C=CH_2 (10): To a cold (−78 °C) solution of $(Me_3Si)_2CHPCl_2$ (3.07 g, 11.76 mmol) in diethyl ether (100 mL) was added, dropwise, a solution of *n*PrMgCl in diethyl ether (11.76 mL, 23.52 mmol). The solution was allowed to attain room temperature and was stirred for 12 h. Deoxygenated water (50 mL) was added and the organic layer was dried with activated 4-Å molecular sieves. Solvent was removed in vacuo to give (*n*Pr_2P)$(Me_3Si)_2CH$. This phosphane (2.60 g, 9.41 mmol) was dissolved in dichloromethane (10 mL), treated with elemental sulfur (0.30 g, 9.41 mmol) and stirred for 2 h. Solvent was removed in vacuo and the product was dissolved in THF (20 mL), treated with *n*BuLi (3.76 mL, 9.40 mmol) and stirred for 2 h. A large excess of paraformaldehyde (1.41 g, 0.044 mol) was added and this mixture was stirred for 1 h. The reaction was then quenched with deoxygenated water (30 mL) and the organic layer was extracted with diethyl ether (3 × 20 mL) and dried with activated 4-Å molecular sieves. Solvent was removed in vacuo to give **10** as a pale yellow oil. Isolated yield 1.86 g, 65%. ^{1}H NMR ($CDCl_3$, 27 °C): δ = 0.04 (s, 9 H, $SiMe_3$), 0.76−1.55 (m, 14 H, Pr), 6.23 (dd, $J_{H,H}$ = 3, $^3J_{PH}$ = 51 Hz, 1 H, =CH_2), 6.67 (dd, $J_{H,H}$ = 3, $^3J_{PH}$ = 34 Hz, 1 H, =CH_2) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 27 °C): δ = 0.54 ($SiMe_3$), 15.26 (Pr), 16.01 (Pr), 35.17 (Pr), 146.20 (=CH_2) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ = 52.3 ppm.

Preparation of [Ph_2P(S)][*i*Pr_2P(S)]C=CH_2 (11): To a solution of the diphosphane (Ph_2P)(*i*Pr_2P)CH_2 (3.64 g, 11.51 mmol; see **7** above) in dichloromethane (40 mL) was added elemental sulfur (0.738 g, 11.51 mmol) and this solution was stirred for 2 h. Solvent was removed in vacuo and the white solid was dissolved in THF (20 mL), treated with *n*BuLi (4.60 mL, 11.51 mmol) and left to stir for 12 h. The deep orange solution was then added, dropwise, to a cold (−78 °C) solution of chlorotrimethylsilane (1.49 mL, 11.51 mmol) in diethyl ether (10 mL). The solution was allowed to attain room temperature and was treated with a further equivalent of *n*BuLi (4.60 mL, 11.51 mmol) and stirred for 12 h. To the resulting solution was added solid paraformaldehyde (1.63 g, 54.15 mmol) and diethyl ether (20 mL) and the mixture was allowed to stir for 1 h before deoxygenated water (30 mL) was added. The organic phase was decanted, the aqueous layer was extracted into diethyl ether (3 × 10 mL) and the combined organic extracts were dried with activated 4-Å molecular sieves. The solution was filtered and solvent was removed in vacuo to give a colorless oil which yielded **11** as a white crystalline solid on addition of ethanol (20 mL). Isolated yield 2.10 g, 53% (based on Ph_2PMe). $C_{20}H_{26}P_2S_2$ (392.5): calcd. C 61.20, H 6.81; found C 60.51, H 6.81. ^{1}H NMR ($CDCl_3$, 25 °C): δ = 0.72 [dd, $J_{H,H}$ = 7, $^3J_{PH}$ = 19 Hz, 6 H, $CH(CH_3)_2$], 1.08 [dd, $J_{H,H}$ = 7, $^3J_{PH}$ = 19 Hz, 6 H, $CH(CH_3)_2$], 3.07 [m, 2 H, $CH(CH_3)_2$], 6.34 (ddd, $J_{H,H}$ = 1, $^3J_{PH}$ = 22, $^3J_{PH}$ = 37 Hz, 1 H, =CH_2), 7.40−7.50 (m, 6 H, Ph), 7.52 (ddd, $J_{H,H}$ = 1, $^3J_{PH}$ = 22, $^3J_{PH}$ = 37 Hz, 1 H, =CH_2), 7.67−7.71 (m, 4 H, Ph) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ = 17.89 [$CH(CH_3)_2$], 18.18 [$CH(CH_3)_2$], 28.89 [$CH(CH_3)_2$], 128.72, 130.97, 131.84, 136.26 (Ph), 150.93 (=CH_2) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ = 42.4 [d, $J_{P,P}$ = 26 Hz, P(S)Ph_2], 84.0 (d, $J_{P,P}$ = 26 Hz, P(S)*i*Pr_2) ppm.

Preparation of [Ph_2P(S)][Me_2P(S)]C=CH_2 (12): To a solution of trimethylphosphane (2.31 g, 30.66 mmol) in light petroleum (30 mL) was added *t*BuLi (18.04 mL, 30.66 mmol) and this mixture was stirred for 12 h. The resulting precipitate was isolated by filtration, washed with light petroleum (3 × 15 mL) and dried in vacuo. The solid was dissolved in THF (30 mL) and added to a cold (−78 °C) solution of chlorodiphenylphosphane (4.63 mL, 25.81 mmol) in THF (20 mL). The solvent was removed in vacuo to give a straw-colored oil which was dissolved in light petroleum (40 mL) and washed with deoxygenated water (3 × 20 mL). The organic phase was dried with activated 4-Å molecular sieves and solvent was removed in vacuo to give the diphosphane (Ph_2P)(Me_2P)CH_2 as a colorless oil.

To a solution of the diphosphane $(Ph_2P)(Me_2P)CH_2$ (4.74 g, 18.20 mmol) in dichloromethane (40 mL) was added elemental sulfur (1.17 g, 36.40 mmol) and this mixture was stirred for 2 h. Solvent was removed in vacuo and the white solid was dissolved in THF (20 mL), treated with *n*BuLi (6.76 mL, 16.56 mmol) and left to stir for 12 h. The resulting deep orange solution was added, dropwise, to a cold (−78 °C) solution of chlorotrimethylsilane (2.10 mL, 16.56 mmol) in diethyl ether (10 mL). The solution was allowed to attain room temperature and was treated with a further equivalent of *n*BuLi (6.76 mL, 16.56 mmol) and stirred overnight. To the resulting solution was added paraformaldehyde (2.49 g, 82.8 mmol) and diethyl ether (20 mL) and the mixture was stirred for 1 h before deoxygenated water (30 mL) was added. The organic layer was decanted, the aqueous layer was extracted into diethyl ether (3 × 10 mL) and the combined organic extracts were dried with activated 4-Å molecular sieves. The dried solution was filtered and solvent was removed in vacuo to give a colorless oil which yielded **12** as a white crystalline solid on the addition of warm light petroleum. Isolated yield 2.19 g, 40%. ^1H NMR ($CDCl_3$, 25 °C): δ = 1.89 (d, $^2J_{PH}$ = 13 Hz, CH_3), 6.02 (m,1 H, $=CH_2$), 7.41−7.84 (m, 11 H, Ph and $=CH_2$) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ = 23.55 (CH_3), 128.8, 130.3, 131.9 (Ph), 147.8 ($=CH_2$) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ = 42.7 (d, $J_{P,P}$ = 30 Hz, PPh_2), 43.0 (d, $J_{P,P}$ = 30 Hz, PMe_2) ppm.

Reaction between [(*n*Pr$_2$P)(Me$_3$Si)$_2$C]Li and Paraformaldehyde: To a solution of $(nPr_2P)(Me_3Si)_2CH$, prepared as for **6**, (1.07 g, 3.87 mmol) in light petroleum (20 mL) was added *t*BuLi (6.58 mL, 3.87 mmol) and this mixture was stirred for 12 h. To the resulting solution was added THF (10 mL) and solid paraformaldehyde (1.00 g, 33.30 mmol). This mixture was stirred for 1 h and then degassed water (20 mL) was added. The organic layer was decanted and the aqueous phase was extracted into diethyl ether (3 × 10 mL). The combined organic extracts were dried with activated 4-Å molecular sieves and then solvent was removed in vacuo to give a pale yellow oil. Flash distillation of this oil under reduced pressure (20 °C, 10^{-2} Torr) gave **5** as a colorless oil. Spectroscopic data for **5**: ^1H NMR ($CDCl_3$, 24 °C): δ = 1.10−1.45 (m, 14 H, *n*Pr), 5.59 (m, 1 H, $=CH_2$), 5.65 (m, 1 H, CH=), 6.14 (m, 1 H, $=CH_2$) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 24 °C): δ = −28.0 ppm. EIMS (of the sulfide): *m*/*z* = 176.0795 [$C_8H_{17}PS$: 176.0789].

Acknowledgments

The authors gratefully acknowledge the support of the EPSRC and the Royal Society.

[1] For recent reviews see: [1a] J. C. Hierso, R. Amardeil, E. Bentabet, R. Broussier, B. Gautheron, P. Meunier, P. Kalck, *Coord. Chem. Rev.* **2003**, *263*, 143. [1b] H. A. Meyer, W. C. Kaska, *Chem. Rev.* **1994**, *94*, 1239.
[2] [2a] W.-J. Peng, S. G. Train, D. K. Howell, F. R. Fronczek, G. G. Stanley, *Chem. Commun.* **1996**, 2607. [2b] M. E. Broussard, B. Juma, S. G. Train, W. J. Peng, S. A. Laneman, G. G. Stanley, *Science* **1993**, *260*, 1784. [2c] G. Süss-Fink, *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 67; *Angew. Chem.* **1994**, *106*, 71.
[3] R. J. Puddephatt, *Chem. Soc. Rev.* **1983**, *12*, 99.
[4] W. Clegg, K. Izod, W. McFarlane, P. O'Shaughnessy, *Organometallics* **1998**, *17*, 5231.
[5] I. J. Colquhoun, W. McFarlane, *J. Chem. Soc., Dalton Trans.* **1982**, 1915.
[6] M. B. Goli, S. O. Grim, *Tetrahedron Lett.* **1991**, *32*, 3631.
[7] For a recent review see: L. F. van Staden, D. Gravestock, D. J. Ager, *Chem. Soc. Rev.* **2002**, *31*, 195.
[8] [8a] A. Mahadevan, P. L. Fuchs, *Tetrahedron Lett.* **1994**, *35*, 6025. [8b] A. Orita, N. Yoshioka, J. Otera, *Chem. Lett.* **1997**, 1023.
[9] M. Mikolajczyk, P. Balczewski, *Synthesis* **1989**, 101.
[10] D. J. Peterson, *J. Org. Chem.* **1968**, *33*, 780.
[11] [11a] Y. Zanella, S. Berte-Verrando, R. Diziere, P. Savignac, *J. Chem. Soc., Perkin Trans. 1* **1995**, 2853. [11b] R. Waschbusch, J. Carran, P. Savignac, *Tetrahedron* **1996**, *52*, 14199. [11c] R. Diziere, P. Savignac, *Tetrahedron Lett.* **1996**, *37*, 1783.
[12] [12a] H. Al-Badri, E. About-Jaudet, J.-C. Combret, N. Collignon, *Phosphorus, Sulfur, and Silicon* **1996**, *111*, 120. [12b] H. Al-Badri, E. About-Jaudet, N. Collignon, *Tetrahedron Lett.* **1996**, *37*, 2951.
[13] B. T. Grobel, D. Seebach, *Chem. Ber.* **1977**, *110*, 852.
[14] Y. Gourdel, A. Ghanami, M. Le Corre, *Tetrahedron Lett.* **1993**, *34*, 1011.
[15] F. A. Carey, A. S. Court, *J. Org. Chem.* **1972**, *37*, 939.
[16] M. J. S. Gynane, A. Hudson, M. F. Lappert, P. P. Power, H. Goldwhite, *J. Chem. Soc., Dalton Trans.* **1980**, 2428.
[17] S. Hietkamp, H. Sommer, O. Stelzer, *Inorg. Synth.* **1989**, *25*, 120.

Received October 28, 2003

