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Catalyst-Free and Catalysed Addition of P(O)–H Bonds to Allenyl/Alkynyl-Phosphonates and -Phosphane Oxides: Use of a Robust, Recoverable Dinuclear Palladium(I) Catalyst

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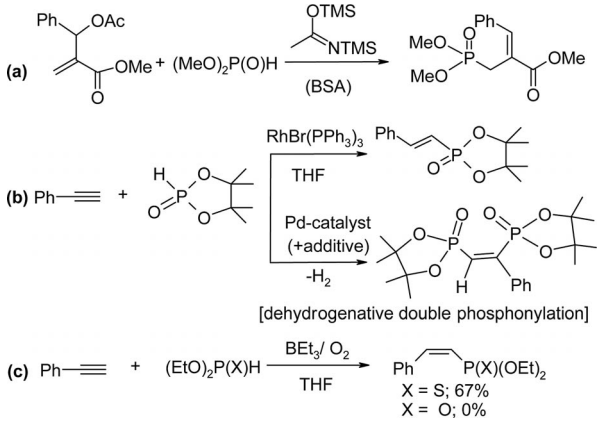
An effective, recoverable, dinuclear palladium(I) catalyst $[(OCH_2CMe_2CH_2O)PSPd(PPh_3)]_2$ has been explored and compared with other traditional palladium catalysts (e.g., $[Pd(PPh_3)_4]$) in the phosphonylation/phosphanylation of allenes $(OCH_2CMe_2CH_2O)P(O)CH=C=CH_2$ (**1**), $Ph_2P(O)$-$CH=C=CH_2$ (**2**), $(EtO)_2P(O)CH=C=CH_2$ (**3**) $(OCH_2$-$CMe_2CH_2O)P(O)CH=C=CMe_2$ (**4**), $Ph_2P(O)CH=C=CMe_2$ (**5**), $(OCH_2CMe_2CH_2O)P(O)C(Ph)=C=CH_2$ (**6**) and $Ph_2P(O)$-$C(Ph)=C=CH_2$ (**7**). The phosphonylation/phosphanylation, in general, occurred at the carbon β to the phosphorus atom, but the concomitant proton addition took place at the α or γ positions leading to either allyl- or vinyl-phosphonates. The use of $P(n\text{Bu})_3$ as catalyst led to geminal and bis-phosphonylation/phosphanylation with less substituted $=CH_2$ terminal allenes **1** and **2**. In conjunction with the use of the corresponding isomeric alkynes **8** and **9**, as many as five different types of phosphonylated products have been synthesized. The reactions with the more substituted allenes **4**–**7** gave single products in most cases. Several examples of catalyst-free, solvent-free phosphanylation reactions are also described. The reactivity of the phosphonylating/phosphanylating agents was found to be $(OCH_2CMe_2CH_2O)P(O)H$ (**10**) < $(OCH_2CMe_2CH_2O)P(S)H$ (**11**) < $Ph_2P(O)H$ (**12**) ≈ $Ph_2P(S)H$ (**13**). The catalytic activity of the recoverable dinuclear palladium(I) complex $[(OCH_2CMe_2CH_2O)PSPd(PPh_3)]_2$ (**14**), which poses interesting questions about the mechanistic pathway, is briefly highlighted. Structures of the dinuclear palladium(I) catalyst **14** and the key products were determined by X-ray crystallography.

Introduction

A variety of unsaturated organic systems undergo hydrophosphonylation/phosphanylation to yield a diverse class of organophosphonates including vinyl/allylphosphonates.[1] Because organophosphonates are of great synthetic utility and exhibit biological activity,[2] we have become interested in this class of compounds.[3] Although there are examples of P–C bond-forming reactions conducted under catalyst-free conditions,[1i,4] in the majority of cases transition-metal catalysts,[5] radical initiators,[6] strong bases or Lewis acids, or microwave (MW) assistance[7] are employed. Significant success has been achieved in these reactions and a selection of examples are shown in Scheme 1.[8]



Scheme 1.

In a recent paper we showed that hydrophosphonylation can also be activated via pentacoordinate phosphorus species through the use of tetrabutylammonium fluoride in an ionic liquid medium;[9] the involvement of P–F-bonded pentacoordinate phosphorane[10] in this reaction was established by a combination of ^{31}P, ^{19}F and ^{1}H NMR spectroscopy. Double phosphonylation has also been reported in some cases.[7c,8f,11] In the reactions described above, the substrates are generally alkenes or alkynes; reports of reactions using allenes[12] are rather rare and only a few examples are available.[13] Our interest in this connection was primarily to explore the phosphonylation/phosphanylation of inexpensive allenylphosphonates/allenylphosphane oxides such as **1**–**7**[3e,14] under different conditions and, where possible, to compare these with the reactions of alkynes (e.g., **8** and **9**).[15] We have restricted the phosphonylating/phos-

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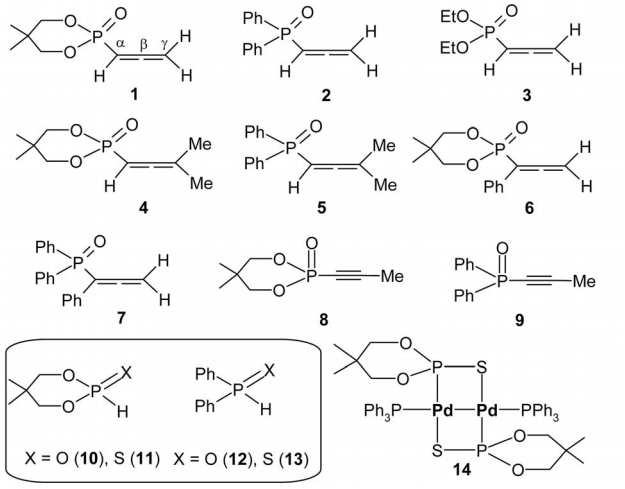
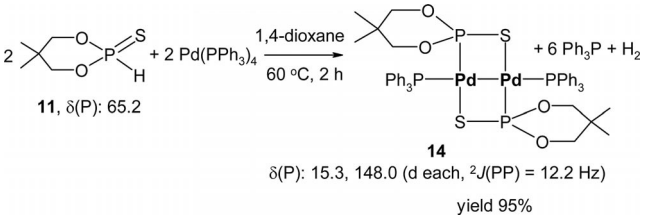
phanylating agents to **10**–**13** for ease of comparison. Note that the attack of the phosphorus moiety in the phosphonylation/phosphanylation can take place at the α, β or γ position of the allene (cf. structure **1**). In comparison with the alkynes (cf. **1** and **8**), we were also curious to know whether or not dehydrogenative phosphonylation [cf. Scheme 1 (c)][8f] occurs in our system. Finally, we report the isolation of the dinuclear palladium(I) complex **14**, which acts as a "recoverable" catalyst; this, we believe, has some relevance to the mechanism because in a large number of palladium-catalysed reactions the initial palladium compound [e.g., $[Pd(PPh_3)_4]$ or $Pd(OAc)_2$] acts only as a "procatalyst" and is not recovered subsequent to the reaction. We report these results herein.



Results and Discussion

Formation/Synthesis of the Dinuclear Palladium(I) Compound 14

The dinuclear palladium(I) compound **14** was initially obtained as a precipitate in a hydrothiophosphonylation reaction. Subsequently, an easier direct route (Scheme 2) provided the compound in excellent yield (95%). Although similar compounds have been described in the literature,[16] we are not aware of any report concerning their use in catalytic reactions. This compound shows only a doublet of doublets with a low *J*(P,P) value of 12.2 Hz in the ^{31}P NMR spectrum, similar to that reported in the literature, and the X-ray structure (Figure 1, see Supporting Information for details) clearly establishes the presence of a dinuclear motif



Scheme 2.

with a Pd–Pd distance of 2.607(1) Å.[16c,17] This type of reaction involving dihydrogen elimination has previously been discussed by Walther et al. and hence is not elaborated here.[16a]

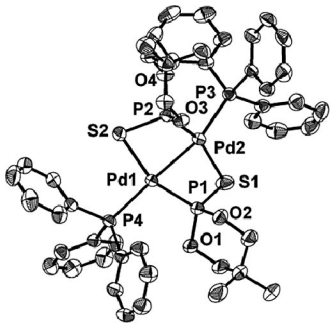
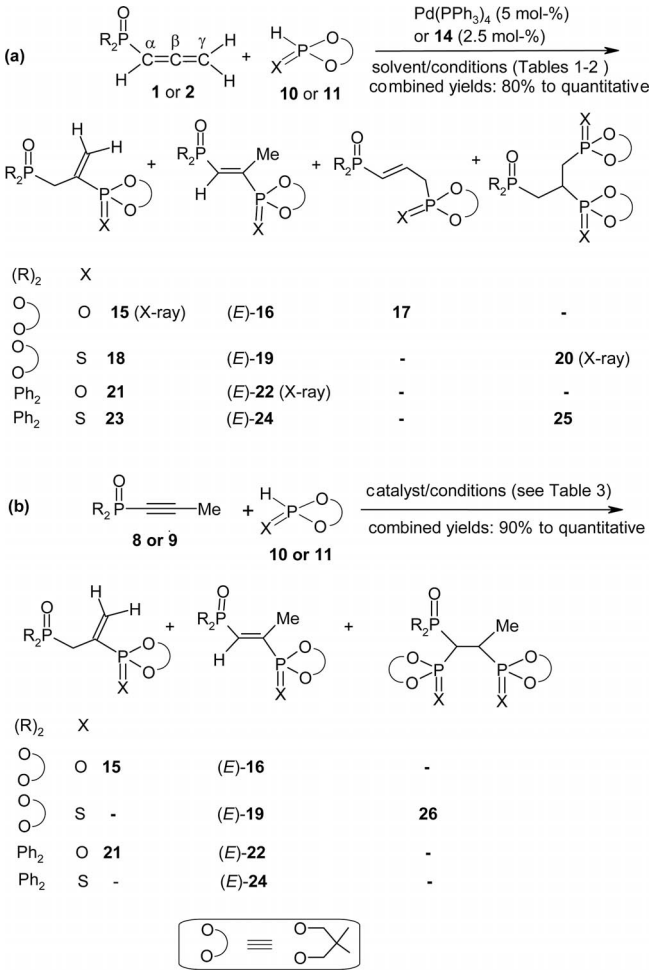


Figure 1. ORTEP diagram of **14**·$2C_4H_8O_2$. Solent molecules have been omitted for clarity. Selected bond lengths [Å] with estimated standard deviations in parentheses: Pd1–Pd2 2.607(1), Pd1–P1 2.211(1), Pd1–P4 2.323(1), Pd1–S2 2.398(1), Pd2–P2 2.206(1), Pd2–P3 2.317(1), Pd2–S1 2.385(1), P1–S1 2.017(2), P2–S2 2.016(2).

Reactions of Allenes $R_2P(O)C(H)=C=CH_2$ [R_2 = $OCH_2CMe_2CH_2O$ (1), R = Ph (2), OEt (3)] and Alkynes $R_2P(O)C{\equiv}CCH_3$ [R_2 = $OCH_2CMe_2CH_2O$ (8), R = Ph (9)] with $R'_2P(X)H$ [R'_2 = $OCH_2CMe_2CH_2O$, X = O (10) or S (11); R′ = Ph, X = O (12) or S (13)]

The reaction of allene **1** with the cyclic H-phosphonate **10** was conducted first in the presence of $[Pd(PPh_3)_4]$ [Scheme 3 (a), Table 1], which yielded the products **15**–**17**. Among the solvents used, the best combined yield was obtained in 1,4-dioxane. Hence this solvent was employed in subsequent reactions. There was no reaction in the absence of $[Pd(PPh_3)_4]$. Also, the reaction did not proceed in the presence of bases like Et_3N, KO*t*Bu or K_2CO_3. The compounds are readily distinguishable by ^{31}P NMR spectroscopy. A lower ^3J(P,P) value for **15** (27.5 Hz) is consistent with three intervening single bonds whereas a large ^3J(P,P) value in **16** (99.2 Hz) is due to *trans* coupling. The long-range coupling constant ^4J(P,P) for **17** (7.2 Hz) is very small, as expected. The identity of the major product **15** was further confirmed by X-ray crystallography (see Figure S1 of the Supporting Information). The allylphosphonate **15** and the vinylphosphonate **16** result from β attack of the H-phosphonate followed by proton addition at the α or γ position, respectively. The third product **17**, although obtained in a lower yield, was rather unexpected and was formed by attack of the H-phosphonate residue at the γ position. This compound should have formed only from the allene **1** [i.e., not after rearranging to the phosphono-alkyne $(OCH_2CMe_2CH_2O)P(O)C{\equiv}CMe$ (**8**)]. The use of $P(nBu)_3$[8c] as a catalyst in this reaction did not afford any identifiable product. Interestingly, although other palladium compounds like $PdCl_2$, $Pd(OAc)_2$, $[PdCl_2(PPh_3)_2]$, $[Pd_2(dba)_3]$ (dba = dibenzylideneacetone) and $[PdCl_2(PhCN)_2]$/methyl acrylate[8f] were not effective in this transformation, the dinuclear palladium(I) complex

$[(OCH_2CMe_2CH_2O)PSPd(PPh_3)]_2$ (**14**) was fairly effective (Table 1, entry 6) and produced mainly **15** and **16** (combined yield 95%; ratio 2:3). Equally significant is the fact that the palladium complex (**14**) could be recovered (see the Supporting Information) from the reaction mixture, whereas $[Pd(PPh_3)_4]$ could not be recovered. Thus, **14** is a true "catalyst" (or at least resting form of the catalyst) whereas the latter is only a "pro-catalyst". From our point of view, this observation has important implications for the mechanistic role played by palladium compounds in such reactions. We also conducted the reaction of $(EtO)_2P(O)$-$C(H)=C=CH_2$ (**3**) with $(OCH_2CMe_2CH_2O)P(O)H$ (**10**). Although we could identify products similar to **15**–**17** (see the Supporting Information), the isolation of individual compounds by chromatography/crystallization/distillation was not successful in our hands.



Scheme 3.

In contrast to the above, allene **1** reacted with the thio-H-phosphonate $(OCH_2CMe_2CH_2O)P(S)H$ (**11**) quantitatively to give both the mono- (**18**) and bis-phosphonylated (**20**) products [Scheme 3 (a)] along with minor quantities of **19**. Compound **11** is more reactive than **10** in the phosphonylation reaction. The greater reactivity of compounds bearing the P(S)H functionality compared with those with P(O)H has been noted earlier by other workers.[6f] Compound **18** is similar in structure to compound **15** discussed above. It has a terminal double bond and readily undergoes further phosphonylation with **11** leading to the tris-phosphonate **20** (see Figure S2 of the Supporting Information for the X-ray structure). Unlike the reaction with **10**, we did not observe any product similar in structure to **17**. Taking into account the fact that there is bis-phosphonylation, the reaction is essentially quantitative with all the thio-H-phosphonate **11** reacting and some of the remaining allene converting into the alkyne **8**. Addition of more compound **11** (2 mol equiv. with respect to **1**) increased the yield of **20** as expected. Catalyst **14** or $P(n\text{Bu})_3$ also led to the same products (^{31}P NMR) but along with some alkyne **8**. This is expected because we used a 1:1 stoichiometry and the unreacted allene isomerized to the less reactive alkyne **8**.

Table 1. Effect of solvent on the palladium-catalysed reaction of allene **1** with H-phosphonate **10** [Scheme 3 (a)].[a]

Entry	Solvent	T [°C]	t [h]	Ratio of **15/16/17**			Combined yield[b] [%]
1	toluene	110	24	1.5	1.2	1.0	37
2	DMF	100	6	2.3	1.3	1.0	46
3	CH_3CN	80	14	3.0	1.5	1.0	55
4	THF	65	14	2.5	1.0	1.0	45
5	1,4-dioxane	100	6	4.0[c]	2.2[c]	1.0[c]	95
6	1,4-dioxane	100	6	2.0	3.0	–	95

[a] $[Pd(PPh_3)_4]$ was used as the catalyst/pro-catalyst for entries 1–5; for entry 6, catalyst **14** was used. [b] Yields were calculated using ^{31}P NMR spectroscopy. [c] The isolated yields are, respectively, 40, 22 and 10%.

Table 2 and Scheme 3 (a) show the results of the reactions of allenylphosphane oxide **2** with **10** and **11**. The products are **21**–**25**. The X-ray structure of **22** was determined (see Figure S3 of the Supporting Information). The main difference between the reactions of H-phosphonate **10** with **1** or **2** is that in the latter case, a γ,β-addition product analogous to **17** was not isolated. Compounds **14** and $[Pd(PPh_3)_4]$ are the most effective catalysts/pro-catalysts. The yield of the bis-phosphonylated product **25**, which is similar in structure to **20**, could be optimized to 90% by increasing the stoichiometry of the thio-H-phosphonate **11** (2 mol equiv. with respect to **2**). In the reaction of **2** with **11** (using **14** as the catalyst) we recovered catalyst **14** and reused it (see the Supporting Information). The reaction of $(EtO)_2P(O)C(H)=C=CH_2$ (**3**) with **11** led to similar products (see Supporting Information) but because of the similarities in the R_f values, pure products could not be isolated.

To fully unravel the synthetic potential as well as the reaction pathway, we also treated the alkyne $(OCH_2CMe_2CH_2O)P(O)C{\equiv}CCH_3$ (**8**) with $(OCH_2CMe_2CH_2O)P(O)H$ (**10**) in the presence of catalytic amounts of $[Pd(PPh_3)_4]$ or palladium complex **14**. In the former case, only compound **16** was obtained in a very clean reaction, whereas with the latter the isomeric compounds **15** and **16** (3:2 ratio by ^{31}P NMR) were obtained quantitatively, again in essentially a very clean reaction [Scheme 3 (b)]. This suggests that the reactions of allene **1** or alkyne **8**[18] with cyclic H-phosphonate **10** using the catalyst **14** may involve some common

Table 2. Reactions of **2** with **10** and **11** leading to the formation of **21** and **22** and **23** and **24**, respectively [cf. Scheme 3 (a)].[a]

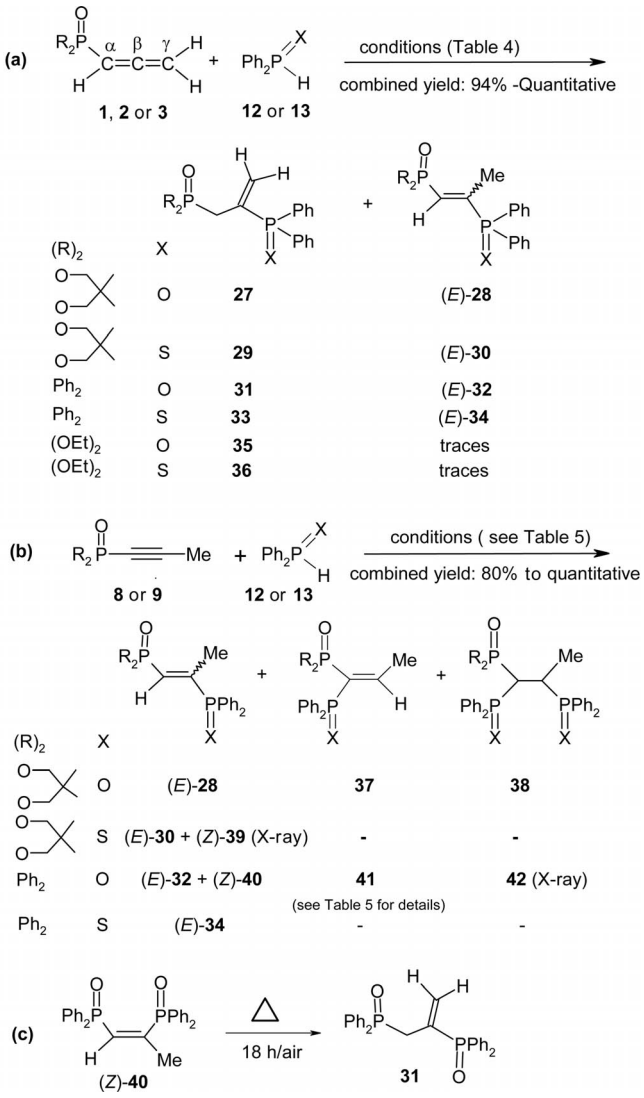
Entry	Pd catalyst	X	Time [h]	Combined yield [%][b]	Ratio **21/22** or **23/24**
1	none	O	36	n.r.	–
2	$Pd(OAc)_2$	O	36	36	1:0
3	$[Pd_2(dba)_3]$	O	36	40	3:2
4	$[Pd(PPh_3)_4]$	O	10	80	3:2
5	**14**	O	12	80	5:1
6	none	S	36	50	1:0
7	$Pd(OAc)_2$	S	36	70	17:1
8	$[Pd_2(dba)_3]$	S	36	60	9:1
9	$[Pd(PPh_3)_4]$	S	4	90[c]	3:1[d]
10	**14**	S	4	90[c]	3:1[d]

[a] All reactions were conducted at 100 °C (oil-bath temperature). [b] Based on ^{31}P NMR analysis. [c] Combined yield of **23**, **24** and **25**. [d] The ratio of **25**/(**23** + **24**) was 3:5 based on the stoichiometry of 1:1.1 for **2**/**11**. The rest was starting material as a result of the bis-phosphonylated product **25**. The yield of **25** could be optimized by adding more of **11** (2 mol equiv. with respect to **2**).

Table 3. Details of the reactions of **8**/**9** with **10**/**11** leading to compounds **15**/**16**, **19**, **21**/**22**, **24** and **26** [cf. Scheme 3 (b)].

Entry	Reactants	Conditions/ duration [h][a]	Product(s)[b] (ratio)	Combined yield [%][c]
1	**8** + **10**	i/6	**16**	quantitative
2	**8** + **10**	ii/6	**15** + **16** (3:2)	quantitative
3	**8** + **11**	i or ii/5	**19**	quantitative
4	**8** + **11**	iii/1	**26**	quantitative
5	**9** + **10**	i/6	**21**	90
6	**9** + **10**	ii/7	**21** + **22** (3:2)	90
7	**9** + **11**	i or ii/8	**24**	90

[a] Conditions i: $[Pd(PPh_3)_4]$ (5 mol-%)/1,4-dioxane, 100 °C. Conditions ii: catalyst **14** (2.5 mol-%)/1,4-dioxane, 100 °C. Conditions iii: $P(nBu)_3$ (20 mol-%)/EtOH, reflux. [b] Isolated yields of individual compounds are given in the Supporting Information (because different methods gave different ratios of the products). [c] Based on ^{31}P NMR spectroscopy.



Scheme 4.

intermediates (see below). There was no reaction in the absence of the catalyst. The behaviour of alkyne **9** was similar to that of **8**. Thus, in its reaction with **10**, a single isomer **22** was obtained by using $[Pd(PPh_3)_4]$ whereas an isomeric mixture of **21** and **22** was obtained in a 3:2 ratio (^{31}P NMR) by using **14** as the catalyst.

The reaction of alkyne **8** with $(OCH_2CMe_2CH_2O)P(S)H$ (**11**) was distinctive. In the presence of $[Pd(PPh_3)_4]$ or **14**, we obtained only the *E*-phosphonylated alkene **19** [Scheme 3 (b), Table 3]. More interestingly, the $P(nBu)_3$/ethanol-catalysed reaction[8c] led to the bis-phosphonylated product **26**, which is different to **20**! The yield of **26** could be enhanced by adding more **11** (2 mol equiv. with respect to **8**). In the assignment of structures **20** and **26**, it must be noted that *J*(P,P) values could vary and in specific cases could be close to zero (see the Supporting Information for the X-ray structure of an analogous compound). Hence the expected multiplet pattern was not seen. The reaction of alkyne **9** with **11** under palladium-catalysed conditions led to the single product **24**. Thus, three different types of phosphonylated products, **15**/**21**, **16**/**22** and **26**, were isolated in this set of reactions by using alkyne **8** or **9** and H-phosphonate/thio-H-phosphonate **10** or **11**.

The reactions of allene **1** with $Ph_2P(X)H$ [X = O (**12**), S (**13**)] did not require the use of a catalyst [Scheme 4 (a), Table 4]. Although we used the palladium complexes initially, this was found to be unnecessary in these cases, which shows that **12** and **13** are significantly more reactive than **10** and **11** in the mono-phosphanylation reaction with **1**. There was no reaction at room temp. either in the presence or in the absence of the catalyst. The overall yields were excellent (quantitative, by ^{31}P NMR). In the reaction with **12**, isomeric β-phosphanylated products **27** and **28** were obtained; neither a γ-phosphanylated product similar to **17** nor a bis-phosphanylated derivative was observed. With $Ph_2P(S)H$ (**13**), compound **29** was the sole product isolated; only a minor amount (10%, ^{31}P NMR) of isomer **30** was present in the reaction mixture. The reaction using $P(nBu)_3$ was not clean but contained **27** and **28** (or **29** and **30**) along with the alkyne **8** (^{31}P NMR).

Table 4. Details of the reactions of allenes **1**, **2** or **3** with **12** or **13** leading to compounds **27**–**36** [cf. Scheme 4 (a)].[a]

Entry	Reactants	Product(s)[b] [ratio]	Combined yield [%][c]
1	**1** + **12**	**27** + **28** [9.2:0.8]	quantitative
2	**1** + **13**	**29** + **30** [9:1]	quantitative
3	**2** + **12**	**31** + **32** [9.5:0.5]	quantitative
4	**2** + **13**	**33** + **34** [9.2:0.8]	quantitative
5	**3** + **12**	**35**	94
6	**3** + **13**	**36**	98

[a] Conditions: no catalyst, no solvent, 100 °C, 1 h. [b] Isolated yields of the individual compounds **27**–**36** are given in the Supporting Information. [c] Based on ^{31}P NMR spectroscopy.

The reactions of allenylphosphane oxide $Ph_2P(O)$-C(H)=C=CH_2 (**2**) with $Ph_2P(X)H$ [X = O (**12**), S (**13**)] led to the β,α (**31** or **33**) or β,γ-*E* (**32** or **34**) isomers [see Scheme 4 (a), Table 4]. We did not observe $Ph_2P(O)OH$ (by oxidation of **12**) in these reactions. For comparative purposes, we also carried out the hydrophosphanylation of the allene $(EtO)_2P(O)C(H)=C=CH_2$ (**3**) with $Ph_2P(X)H$ [X = O (**12**), S (**13**)]. These reactions afforded essentially the β,α-P(X)–H addition products **35** and **36** [cf. Scheme 4 (a)]. Thus, these results are similar to those obtained by using allene **1**.

In the reactions of alkyne **8** with **12** or **13** under palladium-catalysed conditions in 1,4-dioxane, a single product (**28** or **30**, respectively) was obtained almost exclusively [Scheme 4 (b), Table 5]. In contrast, under P(*n*Bu)$_3$-catalysed conditions, in the reaction of **8** with **12** the bis-phosphanylated product **38** was the major product along with the corresponding geminal isomer **37**. The product **38** is similar to **26** obtained from the reaction of **8** with $(OCH_2CMe_2CH_2O)P(S)H$ (**11**), as shown in Scheme 3. However, analogous geminal products were not seen when $Ph_2P(S)H$ (**13**) was used. Here, the products (total yield 88%) were (*E*)-**30** and (*Z*)-**39** (see Figure S4 in the Supporting Information for the X-ray structure). Overall, five different types of phosphanylated products (**27**/**29**, **28**/**30**, **37**, **38** and **39**) were obtained in this set of reactions using allene **1** or its alkyne isomer **8**.

Table 5. Details of the reactions of alkynes **8** or **9** with **12** and **13** leading to compounds **28**, **30**, **32**, **34**, **37**–**42** [cf. Scheme 4 (b)].

Entry	Reactants	Condition/ duration [h][a]	Product(s)[b] [ratio]	Combined yield [%][c]
1	**8** + **12**	i/8	**28**	quantitative
2	**8** + **12**	ii/1	**37**[d] + **38** [1:2]	90
3	**8** + **13**	i/6	**30**	quantitative
4	**8** + **13**	ii/1	**30** + **39** (X-ray) [2:3]	88
5	**9** + **12**	iii/1	**32** + **40** [3:2]	quantitative
6	**9** + **12**	ii/1	**41**+ **42** (X-ray) [1:3]	80
7	**9** + **13**	i/6	**34**	95
		ii/1	**34**	82

[a] Conditions i: [$Pd(PPh_3)_4$] (5 mol-%) or **14** (2.5 mol-%)/1,4-dioxane, 100 °C. Conditions ii: P(*n*Bu)$_3$ (20 mol-%)/EtOH, reflux. Conditions iii: Solvent-free, catalyst-free, 100 °C. [b] The isolated yields of individual compounds are given in the Supporting Information. [c] Based on ^{31}P NMR spectroscopy. [d] Although compound **38** could be easily separated, the minor component **37** was obtained along with (O)P(*n*Bu)$_3$.

In contrast to the above, the reaction using alkyne **9** and $Ph_2P(O)H$ (**12**) under solvent-free and catalyst-free conditions afforded the isomers (*E*)-**32** and (*Z*)-**40** [Scheme 4 (b), Table 5]. More importantly, compound (*Z*)-**40** isomerized to the β,α product **31** upon further heating [Scheme 4 (c)]. This process could be conveniently monitored by ^{31}P NMR spectroscopy (Figure 2). To the best of our knowledge, such an isomerization has not been recorded in the literature. As regards compound **32**, thermodynamic factors may be responsible for its resistance to a similar isomerization.

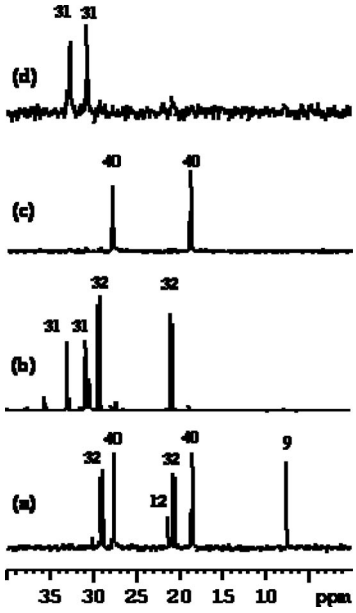
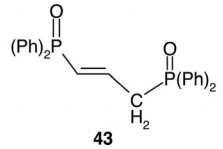


Figure 2. ^{31}P NMR spectra of (a) **9** with $Ph_2P(O)H$ (**12**) under solvent-free, catalyst-free conditions at 100 °C after 30 min, (b) **9** with $Ph_2P(O)H$ (**12**) under solvent-free, catalyst-free conditions at 120 °C after 18 h, (c) the pure *Z* isomer **40** and (d) compound **31** obtained by heating **40** at 120 °C for 18 h.

The P(*n*Bu)$_3$-catalysed reaction of alkyne **9** with $Ph_2P(O)H$ (**12**) afforded only the geminal products **41** and **42**, thus providing an altogether new set of compounds [Scheme 4 (b), Table 5]. The structure of the bis-phosphanylated product **42** was confirmed by X-ray crystallography (see Figure S5 in the Supporting Information) and suggests that it does not result from the γ-phosphonylated product **43**.[8c] In the reaction of **9** with $Ph_2P(S)H$ (**13**), compound **34** was the predominant product irrespective of the reaction conditions.



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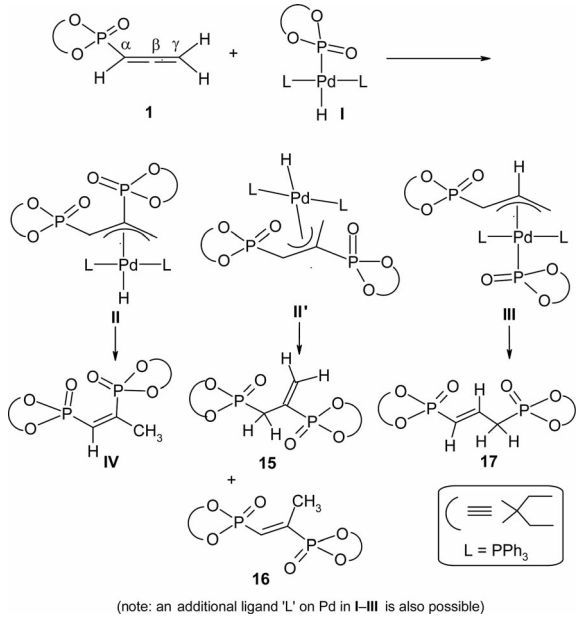
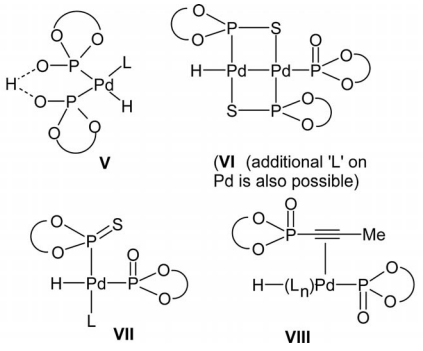
A possible mechanism for the formation of compounds **15**–**17** is shown in Scheme 5. Species **II** and **II′** are analogous to those proposed by Zhao et al.[13a] As can be readily seen, the *Z* alkene **IV** should have been formed, but we could not identify it in the reaction mixture. Note that in lieu of **I**, it is also possible to have an intermediate of type **V**,[19] but this would require 2 mol equiv. of H-phosphonate

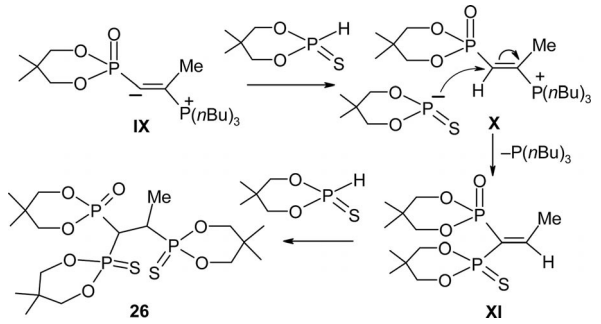
per palladium. What is perhaps more intriguing is the nature of the intermediate obtained with our dinuclear catalyst **14**; a possible structure is **VI** or **VII**. However, at the moment this is only speculation. Because we observed that catalyst **14** can be recovered after the reaction, it is possible that the PPh_3 ligand may still be present on the two palladium centres in the intermediate stages. In any case, the catalytic activity of **14** poses interesting challenges to our understating of these palladium-catalysed reactions. The formation of the γ,β product **17** is possible only from allene **1** and not from its alkyne isomer **8**. In the palladium-catalysed reactions using alkyne **8**, we obtained either **16** or **15** + **16**; a possible intermediate in the latter case is **VIII**.



Scheme 5.



Clearly, the reaction of **1** with the thio-H-phosphonate **11** in the presence of $[Pd(PPh_3)_4]$ should involve the dinuclear palladium(I) complex **14** (cf. Scheme 2) and hence an intermediate similar to **VI** or **VII**. A possible explanation for the formation of the bis-phosphonylated product **20** is that the mono-phosphonylated alkene **18** is more reactive than its precursor **1**. The formation of **19** can be explained in a manner similar to that for **16**. As expected, some of the allene **1** (in the palladium-catalysed reaction) or the isomeric alkyne **8** [in the P(*n*Bu)$_3$-catalysed reaction due to rearrangement] was remaining after 4 h. Previous reports on the P(*n*Bu)$_3$-catalysed reactions of alkynylphosphonates suggest that a geminal phosphonylation/phosphanylation occurs in most cases.[8c] On this basis, the formation of bis-phosphonylated product **26** may be rationalized as shown in Scheme 6 with species **IX** as an intermediate.[20] In the reactions with allene **1**, it is possible that the phosphane attacks the β carbon.[21] The formation of phosphonylated/phosphanylated compounds **21**–**26** may be explained on the basis of the data presented in Schemes 5 and 6. The reactions of allenes **1**–**3** with **12** or **13** under solvent-free, catalyst-free conditions most likely involves a radical mechanism, as discussed elsewhere.[4b] We conducted the reaction of allene **2** with $Ph_2P(S)H$ (**13**) in 1,4-dioxane at 100 °C for 1 h in the absence as well as in the presence of *p*-hydroquinone (10 mol-%). In the former case, the reaction went to completion whereas in the latter case, only around 30% of allene **2** reacted. With 80 mol-% of the *p*-hydroquinone, the reaction was essentially completely inhibited. These observations too suggest a radical mechanism. The palladium- and P(*n*Bu)$_3$-catalysed reactions shown in Scheme 4 may also be rationalized by the discussion presented here.

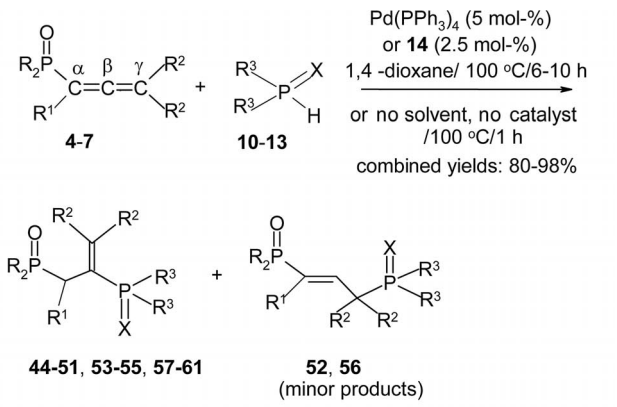


Scheme 6.

Hydrophosphonylation/Hydrothiophosphonylation/Hydrophosphanylation/Hydrothiophosphanylation of the Substituted Allenylphosphonates/Allenylphosphane Oxides $(OCH_2CMe_2CH_2O)P(O)CH=C=CMe_2$ (4), $Ph_2P(O)$-$CH=C=CMe_2$ (5), $(OCH_2CMe_2CH_2O)P(O)$-$C(Ph)=C=CH_2$ (6) and $Ph_2P(O)C(Ph)=C=CH_2$ (7)

In contrast to the reactions with **1** and **2**, the reactions of the substituted allenylphosphonates/allenylphosphane oxides **4**–**7** with **10**–**13** were less complicated and in most cases, the β,α derivatives **44**–**51**, **53**–**55** and **57**–**61** were the major products (Table 6). Of these, **44** and **46** are known compounds.[9] There was no significant difference in the products formed using either $[Pd(PPh_3)_4]$ or **14** in the reactions that we investigated. In several cases (products **53**–**55** and **57**–**61**), the reaction under solvent-free, catalyst-free conditions worked well, in particular, $Ph_2P(O)H$ was quite reactive. One important difference though is that in the palladium-catalysed reactions the γ,β products (e.g., **52** and **56**) were observed as minor products (ca. 10%) but were absent in the reactions conducted under solvent-free, catalyst-free

Table 6. Details of the products **44**–**61** obtained from the reactions of **4**–**7** with **10**–**13**.



Reactants	$(R)_2$	R^1	R^2	$(R^3)_2$	X	Product/s	Yield (NMR)
4 + **10**[a]		H	Me		O	**44**[c]	90
5 + **10**[a]	Ph_2	H	Me		O	**45**	95
6 + **10**[a]		Ph	H		O	**46**[c]	90
7 + **10**[a]	Ph_2	Ph	H		O	**47**	80
4 + **11**[a]		H	Me		S	**48**	85
5 + **11**[a]	Ph_2	H	Me		S	**49**	85
6 + **11**[a]		Ph	H		S	**50**	89
7 + **11**[a]	Ph_2	Ph	H		S	**51** + **52**	90[d]
4 + **12**[b]		H	Me	Ph_2	O	**53**	95
5 + **12**[b]	Ph_2	H	Me	Ph_2	O	**54**	98
6 + **12**[a,e]		Ph	H	Ph_2	O	**55** + **56**	90[d]
7 + **12**[b]	Ph_2	Ph	H	Ph_2	O	**57**	98
4 + **13**[b]		H	Me	Ph_2	S	**58**	95
5 + **13**[b]	Ph_2	H	Me	Ph_2	S	**59**	95
6 + **13**[b,f]		Ph	H	Ph_2	S	**60**	98
7 + **13**[b]	Ph_2	Ph	H	Ph_2	S	**61**	96

[a] These reactions were conducted by using $[Pd(PPh_3)_4]$ as well as palladium(I) catalyst **14**: the yields were the same. [b] These reactions were conducted under solvent-free, catalyst-free conditions. [c] This compound was also prepared by another route.[9] [d] This is the combined yield; the minor product **52** or **56** was obtained in 10% yield (^{31}P NMR). [e] This reaction under solvent-free, catalyst-free conditions gave **55** quantitatively. [f] In this case we did not observe the (γ,β)-phosphanylated product.

conditions. The X-ray structures of **52** and **60** are given in the Supporting Information (Figure S6). The phosphane $P(nBu)_3$ was not an effective catalyst in the reactions that we monitored and hence these data are not included here. The formation of products **44**–**61** may be rationalized on the basis of the discussion presented above.

Further Comments on the Reaction Pathways

The three routes [palladium-catalysed, $P(nBu)_3$-catalysed and catalyst-free] employed herein for the hydrophosphonylation/hydrophosphanylation reactions operate by different mechanistic pathways. Although $[Pd(PPh_3)_4]$ has been widely used, it is likely that palladium intermediates in the reactions of allenes with $(OCH_2CMe_2CH_2O)P(O)H$ (**10**) are different to those formed with $(OCH_2CMe_2CH_2O)$-P(S)H (**11**) because in the latter case the dinuclear compound $[(OCH_2CMe_2CH_2O)PSPd(PPh_3)]_2$ (**14**) is formed whereas in the former case there is no precedence for a similar dinuclear species.

Conclusions

We have accomplished the isolation and structural characterization of as many as five distinct types of products (**27/29**, **28/30**, **37**, **38**, **39**, and **31/33**, **32/34**, **40**, **41**, **42**) in phosphonylation/phosphanylation reactions through the appropriate choice of catalytic conditions and by making use of the facile isomerization of $=CH_2$ terminal allenylphosphonates to phosphonoalkynes, the synthetic utility of a new robust, dinuclear "recoverable" palladium(I) catalyst $[(OCH_2CMe_2CH_2O)PSPd(PPh_3)]_2$ (**14**) has been established. The catalytic activity of this compound implies new reaction (mechanistic) pathways are available for phosphonylation/phosphanylation. We have demonstrated this in a recent paper.[22] The isomerization **40**→**31** of the phosphanylated product reported herein should serve as a caveat in the interpretation of the yields of different products because such a process could have been operative in earlier studies also. The observed reactivity of the phosphonylating/phosphanylating agents $[OCH_2CMe_2CH_2O)P(O)H$ (**10**) < $(OCH_2CMe_2CH_2O)P(S)H$ (**11**) < $Ph_2P(O)H$ (**12**) ≈ $Ph_2P(S)H$ (**13**)] is fairly consistent with the available literature.[6f]

Experimental Section

General: Details on the isolation and spectroscopic and analytical data of individual compounds and instrumental methods are given in the Supporting Information.

CCDC-672231 (for **15**) and -774710 to -774716 (for **14**, **20**, **39**, **22**, **42**, **52**, and **60**, respectively) 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.

Supporting Information (see footnote on the first page of this article): Experimental details, isolation/characterization details, crystal data, additional ORTEP diagrams and the ^{1}H and ^{13}C NMR spectra.

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