Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Molecular Catalysis A: Chemical 226 (2005) 11–21
JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL
www.elsevier.com/locate/molcata

Microwave-assisted solventless single and double addition of $HP(O)Ph_2$ to alkynes

Joshua J. Stone, Robert A. Stockland Jr.*, Jose M. Reyes Jr., James Kovach, Caton C. Goodman, Eric S. Tillman

Department of Chemistry, Bucknell University, Moore Avenue, Lewisburg, PA 17837, USA

Received 15 September 2003; received in revised form 10 September 2004; accepted 11 September 2004
Available online 27 October 2004

Abstract

Microwave radiation has been used to promote the addition of diphenylphosphine oxide to alkynes. The addition reactions were carried out using homogeneous and polymer-supported Group 9 catalysts such as $(PPh_3)_3RhCl$, $[Rh(cod)Cl]_2$, and Rh/supported triphenyl phosphine. Solventless reactions involving terminal alkynes were extremely rapid, and high yields of the alkenylphosphine oxides were obtained in 2 min using microwave radiation. The hydrophosphinylation of internal alkynes such as 4-octyne was also rapid (20 min). For comparison, addition reactions were carried out using conventional heating with the solid supported catalysts. The supported catalyst prepared from oligo(vinyl diphenylphosphine-*co*-vinyl diphenylphosphine oxide-*co*-vinyl chloride) was reused seven times to promote the addition of $HP(O)Ph_2$ to 1-heptyne with >90% conversion obtained in each case.

Keywords: $(PPh_3)_3RhCl$; Solventless reactions; Single addition; Double addition

1. Introduction

The addition of P–H bonds to unsaturated substrates is a valuable transformation due to the large number of applications the resulting compounds have in organic, medicinal, and agricultural chemistry. Classic methods of promoting the addition reaction include the addition of bases or radical initiators [1]. When alkynes are used, the addition reaction often results in mixtures of the monofunctional species as well as 1,1 and 1,2 double addition products [2]. The development of a transition-metal-mediated version of these reactions is attractive due to the ability of transition-metal-containing catalysts to control the regioselectivity and stereoselectivity of a reaction through manipulation of the ligand architecture.

A number of transition-metal-containing complexes promote the hydroamination of alkenes and alkynes; however, hydrophosphinylation reactions have received less attention [3]. Glueck and Pringle investigated the platinum-catalyzed addition of $H\text{-}PR_2$ to activated alkenes such as acrylonitrile [4,5], and Tanaka and co-workers reported the rhodium-catalyzed addition of $HP(O)Ph_2$ to alkynes [6] as well as the hydrophosphorylation of alkenes using a pinacol-derived hydrogen phosphonate [7]. Recently, Deprele and Montchamp have reported the addition of $H_2P(O)OR$ to alkenes [8].

Over the last decade, the use of microwave radiation to accelerate transition-metal-catalyzed reactions has been the subject of an intense amount of research [9,10]. Examples of successful applications include Heck [11], Suzuki [12], and Negishi couplings [13]. In many cases, reaction times can be reduced from hours or days to minutes. Despite the intense interest in this chemistry, the effectiveness of microwave radiation on the transition-metal-catalyzed addition of P–H bonds to unsaturated substrates has rarely been investigated [14]. Additionally, atom efficient and "solvent-free" processes have grown in popularity over the last decade due to the ease of product isolation and the elimination of organic solvents from the reaction [15].

* Corresponding author. Tel.: +1 570 577 1665; fax: +1 570 577 1739.
E-mail address: rstockla@bucknell.edu (R.A. Stockland Jr.).

1381-1169/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.molcata.2004.09.020

Recently, there has been a great deal of interest in the use of supported transition metal complexes as catalysts for organic transformations [16–18]. In many cases, the supported catalysts exhibit high reactivity and are easily separated from the reaction mixture by filtration. Ideally, the recovered catalysts promote subsequent reactions and are "recycled". The use of the same catalyst for multiple reactions is attractive from an economic standpoint due to the high cost of transition metals and supporting ligands.

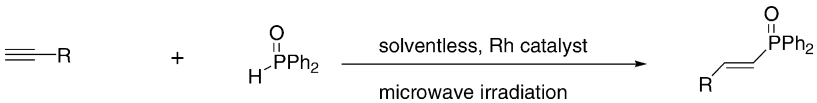
2. Results and discussion

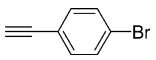
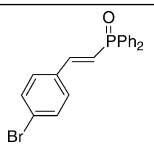
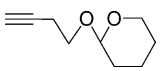
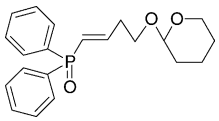
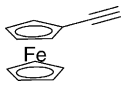
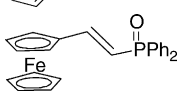
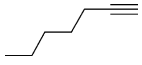
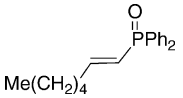
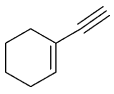
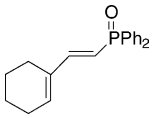
2.1. Solventless reactions involving homogeneous and heterogeneous catalysts

The rhodium-catalyzed addition of $HP(O)Ph_2$ to terminal alkynes was remarkably fast using microwave radiation in the absence of solvent (Table 1). In a typical reaction, a reactor vial was charged with 1 equiv of $HP(O)Ph_2$ and alkyne with 2 mol% Rh as the catalyst. A focused microwave reactor was used to irradiate the samples. When the maximum temperature setting (300 °C) was used as well as the maximum power setting (300 W), an intractable mixture was formed. Decreasing the power and temperature settings to 25 W and 120 °C afforded high yields of the alkenylphosphine oxides in 2 min. In addition to simple alkynes such as phenylacetylene and 1-heptyne, functionalized alkynes such as ethynylferrocene and 4-ethynyl bromobenzene were readily hydrophosphinylated under these conditions. It was encouraging to see that the aryl bromide did not react with rhodium to generate side products. The reaction residues exhibited a single peak in the ^{31}P NMR spectrum that was assigned to the alkenylphosphine oxide. In most cases, the crude product was clean enough to use in subsequent transformations with no further purification. When needed, the rhodium was removed by column chromatography (silica gel).

The use of solid-supported catalysts to promote the addition reaction was also successful. Typically, $HP(O)Ph_2$ was treated with 1 equiv of the desired alkyne using the solid-supported catalyst with no added solvent (Table 1, entries 4 and 5). Reaction times were slightly longer than when $[Rh(cod)Cl]_2$ or $(PPh_3)_3RhCl$ were used (Table 1, entries 1–3). In addition to the desired products, small amounts of double addition products (1–5%) formed when solid-supported catalysts were used. The recovery and reuse of solid-supported catalysts is one of the attractive aspects of the chemistry. The possibility of recycling the catalyst was investigated using 1-heptyne and diphenylphosphine oxide as the model system. After irradiation, the residue was extracted with diethyl ether and filtered. The catalyst was used in three subsequent hydrophosphinylation reactions.

Table 1
Microwave-assisted solventless hydrophosphinylation of terminal alkynes[a]



Entry	Alkyne	Product	Compound	Catalyst, time[b]	Yield[c]
1			**1**	$[Rh(cod)Cl]_2$, 2	87
2			**2**	$[Rh(cod)Cl]_2$, 2	75
3			**3**	$(PPh_3)_3RhCl$, 2	81
4			**4**	i, 7	91
5			**5**	ii, 7	70

[a] Reactions were carried out without solvent using 0.25 mmol alkyne and $HP(O)Ph_2$. Microwave conditions = 25 W, Temp. = 120 °C.
[b] Time is given in minutes.
[c] Yields are based upon isolated material. i = rhodium-bound oligo(vinyl diphenylphosphine-*co*-vinyl diphenylphosphine oxide-*co*-vinyl chloride). ii = rhodium-bound supported triphenyl phosphine.

2.2. Thermal reaction in the absence of catalyst

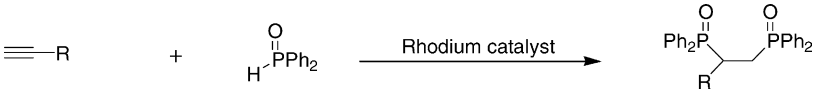
To investigate the possibility that the hydrophosphinylation process was a result of the microwave heating, the addition reaction was carried out using 1-heptyne, phenyl acetylene and ethynylferrocene as model systems. Under the conditions listed in Table 1, only starting materials were recovered after irradiation in the absence of catalyst. Thus, the results shown in Table 1 were due to a metal-catalyzed process.

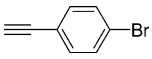
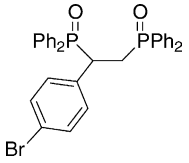
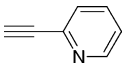
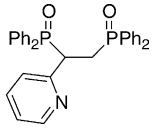
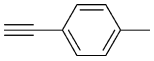
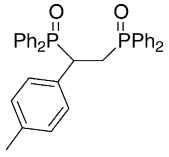
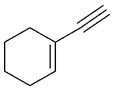
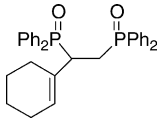
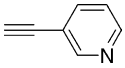
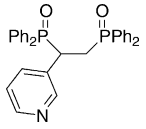
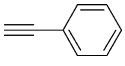
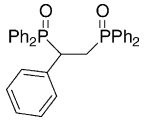
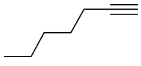
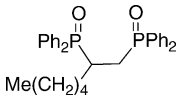
2.3. Double hydrophosphinylation of terminal alkynes

Bisphosphine oxides are important compounds and are used as organocatalysts for the allylation of *N*-acylhydrazones [19]. The synthesis of these compounds is generally cumbersome and requires harsh conditions. In a rare example of a transition-metal-catalyzed process, Lin and co-workers found that homogeneous palladium catalysts promote the double hydrophosphinylation of alkynes [20]. Although successful, the addition process typically required long reaction times (24 h, 110 °C).

To investigate the effectiveness of microwave radiation on the synthesis of bisphosphine oxides, a series of reactions were carried out using the focused microwave reactor with rhodium complexes as catalysts. The results of the reactions are summarized in Table 2. Typically, terminal alkynes were treated with 3 equiv of $HP(O)Ph_2$, and 2 mol% of the catalyst. The reactions were rapid and typically complete within 40 min at 120 °C. In addition to simple alkynes such

Table 2
Microwave-assisted solventless synthesis of bisphosphine oxides[a]



Entry	Alkyne	Product	Compound	Catalyst, time[b]	Yield[c]
1			**6**	$[Rh(cod)Cl]_2$, 40	76
2			**7**	$[Rh(cod)Cl]_2$, 40	84
3			**8**	$(PPh_3)_3RhCl$, 40	64
4			**9**	$[Rh(cod)Cl]_2$, 40	71
5			**10**	$(PPh_3)_3RhCl$, 40	88
6			**11**	i, 40	75
7			**12**	ii, 40	70

[a] Reactions were carried out without solvent using 0.12 mmol alkyne and 0.37 mmol $HP(O)Ph_2$; microwave settings: 50 W, 120 °C.
[b] Time is given in minutes.
[c] Yields are based upon isolated material. i = rhodium-bound oligo(vinyl diphenylphosphine-*co*-vinyl diphenylphosphine oxide-*co*-vinyl chloride). ii = rhodium-bound supported triphenyl phosphine.

as 1-heptyne and phenylacetylene, functionalized substrates such as 4-ethynylbromobenzene and 3-ethynylpyridine were successfully coupled using $[Rh(cod)Cl]_2$ and $(PPh_3)_3RhCl$ as catalysts. It was encouraging to see that the aryl bromide does not react with rhodium to generate side products. Solid-supported catalysts were also successfully used in the double hydrophosphinylation reaction (Table 2, entries 6 and 7). In some cases, analytically pure material could be obtained by simply washing the sample with ethyl acetate/ether (1:1).

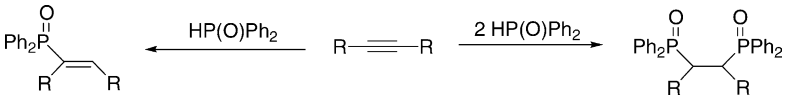
2.4. Mechanistic investigation of the double hydrophosphinylation reaction

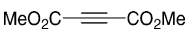
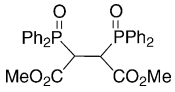
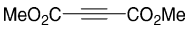
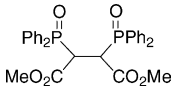
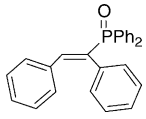
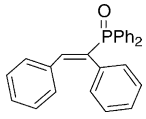
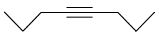
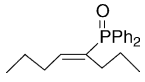
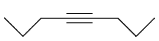
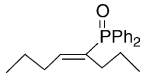
To investigate the possibility that the double-hydrophosphinylation reaction was the result of a radical process, the addition reaction was carried out using several different alkynes in the absence of a catalyst. When unactivated substrates such as phenylacetylene or 3-ethynylpyridine were treated with 3 equiv of $HP(O)Ph_2$ in the absence of solvent and catalyst, only starting materials were recovered after stirring and irradiating for 40 min at 120 °C. However, this result only confirmed that the metal catalyst was needed for the first step in the reaction. This is a critical point because, once the first $–P(O)Ph_2$ group was added, the resulting alkene was activated for the second addition reaction. To investigate if the metal catalyst was critical for the second addition reaction, (*E*)-1-(diphenylphosphinyl)-1-heptene was rigorously purified and used as a representative substrate. Treatment of this compound with 1.5 equiv of $HP(O)Ph_2$ in the absence of solvent and catalyst afforded the double-hydrophosphinylated product in high yield. Thus, the first addition is metal promoted, but the second addition reaction was induced by the microwave radiation.

2.5. Single and double hydrophosphinylation of internal alkynes

Due to the success with terminal alkynes, the microwave-assisted chemistry was extended to internal alkynes. Typically, the alkyne, $HP(O)Ph_2$, and catalyst were added to a microwave reactor vial along with a magnetic stirring bar. The vial was irradiated for 20 min (50 W, 120 °C) in the focused reactor (see Table 3). Similar to the reactions in Tables 1 and 2, no reaction was observed for unactivated substrates in the absence of the metal catalyst. However, when an activated alkyne, dimethyl acetylenedicarboxylate (DMAD), was treated with 2 equiv of $HP(O)Ph_2$ in the presence or absence of a catalyst, the double-hydrophosphinylation reaction occurred to generate the bisphosphine oxide in high yield. Thus, the double hydrophosphinylation of unactivated alkynes proceeds, at least initially, through a metal-catalyzed process, whereas activated internal alkenes were hydrophosphinylated through a microwave-induced reaction.

Table 3
Microwave-assisted solventless hydrophosphinylation of internal alkynes[a]



Entry	Alkyne	Product	Compound	Catalyst, time[b]	Yield[c]
1			**13**	$[Rh(cod)Cl]_2$, 20	73
2			**13**	None, 20	64
3			**14**	$(PPh_3)_3RhCl$, 20	55
4				None, 20	0
5			**15**	i, 20	62
6				None, 20	0

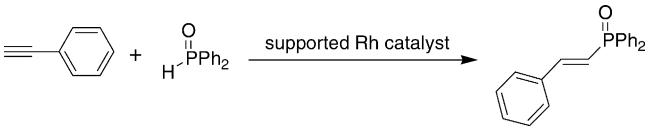
[a] Reactions were carried out without solvent using alkyne $HP(O)Ph_2$; microwave settings: 50 W, 120 °C.
[b] Time is given in minutes.
[c] Yields are based upon isolated material. i = rhodium-bound oligo(vinyl diphenylphosphine-*co*-vinyl diphenylphosphine oxide-*co*-vinyl chloride).

2.6. Addition reactions using solid-supported catalysts with conventional heating

For comparison, a series of addition reactions using solid-supported catalysts were carried out with various solvents and conventional heating. In order to probe the effectiveness of the procedure, the addition of $HP(O)Ph_2$ to phenyl acetylene was used as a model system (Table 4). The use of toluene or THF as the solvent gave high yields of the addition product, while chlorinated solvents ($CHCl_3$, CH_2Cl_2; entries 10 and 11) afforded only 3–5% conversion. High catalyst loadings were successful in promoting reactions at room temperature (entry 10), while lower loadings afforded high conversions at slightly elevated temperatures (entry 7; 75 °C). Concentration was not a key factor in these reactions as evidenced by entries 14–17.

The system selected for catalytic reactions consisted of 1 equiv of alkyne and $HP(O)Ph_2$, 5 mol% of Rh bound polymer, and toluene (2 mL) as the solvent. The results of the addition reactions are summarized in Table 5. Alkynes containing alkyl, aryl, trimethylsilyl, and vinyl groups were consumed within 4 h at 75 °C. The process was high yielding and selective for the *E*-isomer as determined by ^1H NMR spectroscopy. Internal alkynes were also successfully employed (entries 7 and 8), although high yields were only obtained at elevated temperatures (110 °C, 8 h).

Table 4
Reaction conditions for thermal reaction using supported catalyst[a]



Entry	Solvent	Volume (mL)	Temp. (°C)	Loading (mol% Rh)	Time (h)	% Conv.[b]
1	Tol	2	23	1	24	6
2	Tol	2	23	3	24	31
3	Tol	2	23	5	24	56
4	Tol	2	23	10	24	89
5	Tol	2	23	5	16	52
6	Tol	2	40	5	16	69
7	Tol	2	75	5	4	99
8	Tol	2	23	5	24	56
9	THF	2	23	5	24	77
10	$CHCl_3$	2	23	5	24	5
11	CH_2Cl_2	2	23	5	24	5
12	THF/H_2O[c]	2	23	5	24	2
13	THF	0.5	23	5	24	63
14	THF	2.0	23	5	24	77
15	THF	5.0	23	5	24	60
16	THF	10.0	23	5	24	68
17	THF	0.5	23	5	24	63

[a] Reactions were carried out using diphenylphosphine oxide (0.50 mmol) and phenyl acetylene (0.50 mmol).
[b] The conversion was determined by NMR.
[c] 1:1 mixture.

2.7. Catalyst recycling

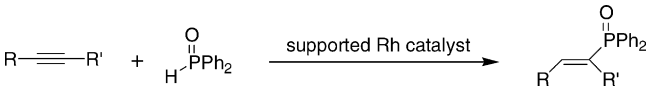
One of the attractive features of a supported catalyst was the ease with which it was separated from the reaction mixture. If the catalyst was recovered, it could conceivably be used in subsequent reactions. We have investigated the recycling of the rhodium-bound oligo(vinyl diphenylphosphine-*co*-vinyl diphenylphosphine oxide-*co*-vinyl chloride) using the addition of $HP(O)Ph_2$ to 1-heptyne as a test case. After completion of the catalytic reaction, the reaction mixture was cooled to room temperature and diluted with toluene (3×8 mL). Separation of the catalyst from the reaction was accomplished by decanting the solution. The solid residue was used as the catalyst for subsequent reactions; however, lower yields of the vinyl diphenylphosphine oxide were obtained (40–50%). The reduction in reactivity could be due to oxidation of the metal from Rh(I) to Rh(III). In an effort to reactivate the catalyst, the residue was refluxed in ethanol for 2 h [21]. After removal of the ethanol, addition reactions using this regenerated catalyst afforded high yields of the vinyl diphenylphosphine oxide. Thus, the procedure for successful reuse of the catalyst consisted of decanting the solution from the solid catalyst, washing the solid with toluene, refluxing in ethanol, and drying under vacuum. Following this protocol, seven reactions were carried out using the same supported catalyst with >90% yields obtained in each case, albeit that longer reaction times were required after the second run.

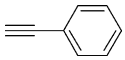
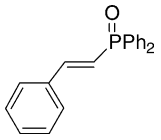
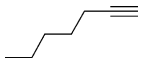
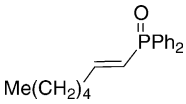
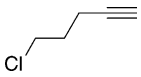
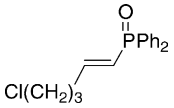
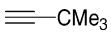
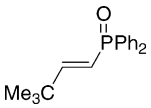
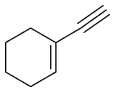
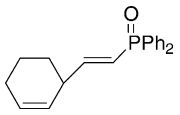
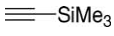
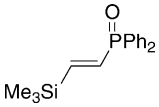
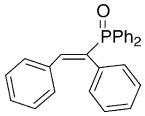
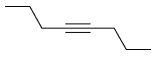
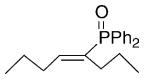
2.8. Rhodium leaching

Although the supported catalyst was successfully reused, the reaction solutions were yellow/red in color. To investigate the possibility of metal leaching from the support, the crude reaction mixtures were analyzed using inductively coupled plasma-atomic emission spectroscopy (ICP-AES; Table 6). The concentration of Rh was highest in the initial reactions and decreased with reuse of the catalyst. The decrease in the amount of Rh in subsequent samples was consistent with the ease of displacement of the metal from different sites on the polymer support (Fig. 1A–D). Rhodium could be displaced from the binding sites containing two phosphine oxides or the hemilabile sites, and less readily from $–PPh_2$ sites. Increasing the temperature of the reaction from 75 to 100 °C did not change the amount of Rh that was leached from the polymer (∼3 μmol of Rh in each case). Additionally, no detectable amounts of Rh were found in the ethanol used in the recycling procedure.

Diphenylphosphine oxide exists as two tautomers, $HP(O)Ph_2$ and $P(OH)Ph_2$. The latter is quite nucleophilic and is known to coordinate to metal centers [22]. To test the possibility of a homogeneous active species created by leaching of the Rh from the solid support, the reaction between $HP(O)Ph_2$ and 1-heptyne was filtered after 5 min (75 °C) and stirred for an additional 4 h (75 °C). Analysis of the reaction products showed that (*E*)-1-(diphenylphosphinyl)hept-1-ene was formed in >90% yield.

Table 5
Addition reactions involving terminal and internal alkynes using conventional heating with a supported catalyst[a]



Entry	Alkyne	Product	Compound	Catalyst, time	Yield[b]
1			**16**	i, 4 h	80
2			**4**	i, 4 h	91
3			**17**	i, 4 h	96
4			**18**	i, 4 h	98
5			**5**	ii, 4 h	92
6			**19**	ii, 4 h	93
7			**15**	i, 8 h	85[c]
8			**16**	ii, 8 h	87[c]

[a] Reactions were stirred at 75 °C for 4 h with 1 equiv. of alkyne (0.50 mmol) and diphenylphosphine oxide (0.50 mmol), supported Rh catalyst (5 mol%), and toluene (2 mL) as the solvent.
[b] Yields are based upon isolated material.
[c] 110 °C, 8 h.

The commercially available "supported triphenylphosphine" was also investigated as the scaffold for these reactions. The Rh-bound material was prepared following literature procedures and screened for activity [23]. As a representative example, the addition of $HP(O)Ph_2$ to 1-heptyne proceeded in 93% yield in 8 h at 75 °C. Similar amounts of Rh were found in the crude reaction mixtures of these reactions (∼1.5 μmol).

2.9. Preparation of the solid-supported catalyst

One of the rhodium-bound solid-supported catalysts was synthesized from commercially available "supported triphenyl phosphine" by treatment of this material with $[Rh(cod)Cl]_2$ and washing with toluene. Preparation of the rhodium-bound oligo(vinyl diphenylphosphine-*co*-vinyl diphenylphosphine oxide-*co*-vinyl chloride) was accomplished in two steps with different sources of starting materials. Treatment of commercial PVC (THF solution; $M_n = 65{,}000$) with $LiPPh_2$ (THF solution prepared from $HPPh_2$ and *n*BuLi; 1:1 per monomer unit), afforded a colorless solid after aqueous workup. The ^{31}P NMR spectrum of this material exhibited two broad resonances of similar intensity (δ −3.0, 29.0 ppm). The resonance at higher frequency was assigned to a $–P(O)Ph_2$ group formed by oxidation of the $–PPh_2$ unit (−3.0 ppm). The chlorine content of the sample decreased from 56.40% (commercial PVC) to 4.72%, showing that a number of the chlorinated sites remained intact (approximately one $–CHClCH_2–$ site for every –6-phosphorus containing sites). This was consistent with

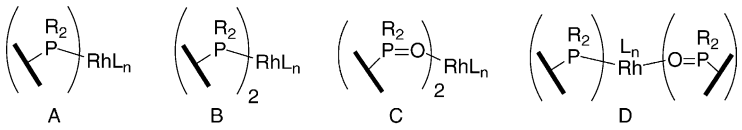


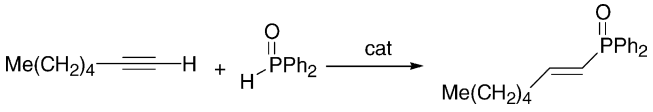
Fig. 1. Coordination of Rh to the solid support.

previous observations that long reaction times at high temperatures were necessary to replace all of chlorine atoms [24,25]. The SEC chromatograph ($CHCl_3$) of the material was multimodal over a wide molecular weight range (M_n = 800–1500) showing that chain scission accompanied the substitution reaction.

Similar results were obtained using a piece of scrap PVC pipe as the source of poly(vinyl chloride). The pipe was shredded, dissolved in THF and precipitated by the addition of methanol (three times) to remove the additives. The colorless PVC was treated with $LiPPh_2$ to afford oligo(vinyl diphenylphosphine-*co*-vinyl diphenylphosphine oxide-*co*-vinyl chloride). The NMR spectra and SEC chromatographs of this material were nearly identical to those obtained using the lower molecular weight PVC. Due to the millions of pounds of PVC that occupy landfills throughout the world, the ability to use waste pipe as the starting material for the preparation of the solid support is both environmentally attractive and cost-effective.

Treatment of oligo(vinyl diphenylphosphine-*co*-vinyl diphenylphosphine oxide-*co*-vinyl chloride) (dissolved in $CHCl_3$) with 0.5 equiv of $[Rh(cod)Cl]_2$ afforded a red/orange solid that precipitated from solution. The volatiles were removed under vacuum, and the resulting residue was washed with ether and dried under vacuum. The solid was used as the catalyst without further purification. Since the polymer support contained both $–P(O)Ph_2$ and $–PPh_2$ pendant groups, several different monodentate and bidentate coordination sites were possible (Fig. 1).

Table 6
Recycling experiments and rhodium leaching[a]



Experiment	Yield (%)[b]	Rh (μmol)[c]	Time (h)	Rh (mol%)[d]
1	91	3.4	4	0.68
2	93	2.8	4	0.56
3	91	1.9	8	0.38
4	92	1.0	12	0.19
5	92	0.7	12	0.14
6	91	0.6	12	0.11

[a] Reactions were stirred at 75 °C with 1 equiv. of 1-heptyne and diphenylphosphine oxide, the same supported Rh catalyst, and toluene (2 mL).
[b] Yields are based upon isolated material.
[c] Determined by ICP-AES.
[d] Relative to the amount of diphenylphosphine oxide.

3. Conclusion

In summary, we have shown that microwave-assisted solventless hydrophosphinylation reactions are remarkably fast and high yielding using homogeneous or solid-supported catalysts. The double hydrophosphinylation of terminal alkynes also proceeds smoothly using microwave radiation. Studies using model systems confirm that the transition metal catalyst is needed for the first addition reaction. However, irradiation alone will promote the second hydrophosphinylation due to the presence of the activating $–P(O)Ph_2$ group. Internal alkynes were also successfully used in the addition reactions. For comparison, hydrophosphinylation reactions were carried out using conventional heating with supported rhodium complexes as the catalysts. The catalyst prepared from oligo(vinyl diphenylphosphine-*co*-vinyl diphenylphosphine oxide-*co*-vinyl chloride) was successfully reused seven times to promote the addition of $HP(O)Ph_2$ to 1-heptyne with >90% conversion obtained in each case.

4. Experimental

4.1. General considerations

All reactions were performed under N_2 using standard Schlenk techniques or in a nitrogen-filled drybox. Reagents including diphenylphosphine, diphenylphosphine oxide, butyllithium, PVC, $[Rh(cod)Cl]_2$, $(PPh_3)_3RhCl$, and alkynes were obtained from Aldrich and used without further purification. THF was distilled from sodium/benzophenone. Dichloromethane, chloroform, and $CDCl_3$ were dried over CaH_2 and distilled. The supported rhodium catalyst prepared from “supported triphenyl phosphine” (Fluka) was generated following literature procedures [23]. Elemental analyses were performed by Midwest Microlabs. The microwave reactions were carried out in a CEM Discover focused reactor using 10 mL heavy-walled reactor vials. The molecular weights of the phosphorus-containing polymers are reported relative to polystyrene standards and were determined by size exclusion chromatography (SEC) using a Waters Breeze SEC system (RI detection; Waters 2414 detector) with $CHCl_3$ as the mobile phase. Due to the low solubility of PVC in $CHCl_3$, THF was used as the eluent for the SEC analysis. ^1H and ^{31}P NMR spectra were recorded at ambient temperature with a Bruker 300-MHZ spectrometer. ^1H NMR chemical shifts are reported relative to $SiMe_4$, and coupling constants are given in Hertz. ^{31}P NMR chemical shifts are reported relative

to external H_3PO_4 (85%, δ 0 ppm). Quantitative ^{31}P NMR spectra were obtained using an inverse-gated decoupling sequence with a recycle delay of 30 s. ICP-AES experiments were carried out on a Thermo Jarrell ICP spectrometer. Samples were prepared for ICP-AES analysis by dissolving the reaction products in concentrated sulfuric acid and diluting with water to a known volume. The crude reaction products (after removing the supported catalyst) were used for the ICP-AES experiments due to reproducibly problems encountered when reaction solutions were tested. The identity and purity of known compounds was established based upon comparison of ^1H and ^{31}P NMR spectra to literature values as well as GC/MS.

4.2. Preparation of oligo(vinyl diphenylphosphine-co-vinyl diphenylphosphine oxide-co-vinyl chloride)

A flask was charged with diphenyl phosphine (2.79 mL, 16.0 mmol) and cooled to −78 °C. THF (10 mL) was added to the flask followed by drop-wise addition of butyllithium (10 mL of 1.6 M solution; 16.0 mmol) to give a bright orange/red solution. A THF (30 mL) solution of PVC (1.0 g, 16.0 mmol) was added by syringe to the $LiPPh_2$ solution with constant stirring. After stirring at 25 °C for 24 h, the reaction was quenched with a few drops of acidic methanol. The product was precipitated by the addition of MeOH to give a white solid that was washed with water and dried under vacuum (3.40 g). Elemental analysis (average of two samples), C: 71.64, H: 6.11, P: 13.44, Cl: 4.42. $^{31}P\{^1H\}$ NMR (25 °C, $CDCl_3$): δ 29.0 (–$P(O)Ph_2$), −3.0 (–PPh_2) ppm.

Note: Due to the pyrophoric nature of secondary phosphines, the commercially available solution of $LiPPh_2$ (Aldrich) is an attractive alternative to the in situ preparation of $LiPPh_2$.

4.3. Preparation of rhodium-bound oligo(vinyl diphenylphosphine-co-vinyl diphenylphosphine oxide-co-vinyl chloride)

A round-bottomed flask was charged with oligo(vinyl diphenylphosphine-*co*-vinyl diphenylphosphine oxide-*co*-vinyl chloride) (0.250 g) and chloroform (15 mL). A chloroform solution of $[Rh(cod)Cl]_2$ (0.270 g, 0.548 mmol) was added by syringe. After stirring 4 h at 25 °C, a red/orange precipitate formed that was collected by filtration, washed with diethyl ether and dried under vacuum (0.365 g).

4.4. General method for the addition reactions

4.4.1. Solventless hydrophosphinylation with microwave heating

A 10 mL heavy-walled glass reactor vial was charged with diphenylphosphine oxide, magnetic stirring bar, alkyne (when the alkyne was a solid), and catalyst (where appropriate). After evacuating the flask and refilling with nitrogen, the alkyne was injected by syringe (when the alkyne was a liquid at room temperature). The reaction mixture was crushed to a fine paste by stirring at room temperature for 5 min and irradiated in a focused microwave reactor. When needed, the title compounds were purified by column chromatography. The identity of known compounds was established by comparison of the ^1H and $^{31}P\{^1H\}$ NMR data to literature values.

4.4.2. Preparation of (E)-1-(diphenylphosphinyl)-2-(4-bromophenyl)ethene (**1**, Table 1, entry 1)

The general procedure was followed using $HP(O)Ph_2$ (0.050 g, 0.25 mmol), 4-ethynylbromobenzene (0.045 g, 0.25 mmol) and $[Rh(cod)Cl]_2$ (0.001 g, 2.0 μmol; 4.0 μmol of Rh). After irradiating for 2 min (maximum power = 25 W, 120 °C), purification of the residue by column chromatography (hexanes/EtOAc) afforded 0.082 g (87%) of the title compound as a colorless solid. Anal. Calcd. for $C_{20}H_{16}BrOP$: C, 62.68; H, 4.21. Found: C, 62.38; H, 4.25. ^1H NMR ($CDCl_3$) δ 7.70–7.62 (m, 4H, Ar–H), 7.50–7.25 (m, 11H, Ar–H, =CH–), 6.75 (dd, 1H, J = 22.1, 17.3, =CH–) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 146.1 (d, J = 3.7, =CH–), 134.0 (d, J = 18.2, quat), 132.6 (d, J = 106.3, *ipso*-C_6H_5), 132.1 (s, Ar–C), 132.0 (d, J = 2.9, Ar–C), 131.3 (d, J = 10.0, Ar–C), 129.2 (s, Ar–C), 128.6 (d, J = 12.2, Ar–C), 124.3 (s, quat), 120.1 (d, J = 103.5, =CH–) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 23.5 (s) ppm.

4.4.3. Preparation of (E)-4-(diphenylphosphinyl)-2-(3-butenyloxy)tetrahydro-2-H-pyran (**2**, Table 1, entry 2)

The general procedure was followed using $HP(O)Ph_2$ (0.050 g, 0.25 mmol), 2-(3-butynyloxy)tetrahydro-2-*H*-pyran (38.8 μL, 0.25 mmol), and $[Rh(cod)Cl]_2$ (0.001 g, 2.0 μmol; 4.0 μmol of Rh). After irradiating for 2 min (max power = 25 W; 120 °C), purification of the residue by column chromatography (hexanes/EtOAc) afforded 0.066 g (75%) of the title compound as an oily solid. Anal. Calcd. for $C_{21}H_{25}O_3P$: C, 70.77; H, 7.07. Found: C: 70.45; H, 7.01. ^1H NMR ($CDCl_3$): δ 7.73–7.67 (m, 4H, Ar–H), 7.55–7.43 (m, 6H, Ar–H), 6.73 (m, 1H, =CH–), 6.35 (dd, 1H, J = 23.7, 17.0, =CH–), 4.59 (m, 1H, –CH–), 3.89 (m, 1H, –CH_2–), 3.78 (m, 1H, –CH_2–), 3.57–3.45 (m, 2H, –CH_2–), 2.64–2.57 (m, 2H, –CH_2–), 1.85–1.40 (m, 6H, –CH_2–) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 149.2 (d, J = 2.4, =CH–), 133.0 (dd, J = 100.6, 4.4, Ar–C), 131.7 (d, J = 2.6, Ar–C), 131.3 (d, J = 10.3, Ar–C), 128.4 (d, J = 12, Ar–C), 124.4 (d, J = 102.6, =CP–), 98.7 (s, –CH–), 65.2 (s, –CH_2–), 62.1 (s, –CH_2–), 34.9 (d, J = 17.0, –CH_2–), 30.5 (s, –CH_2–), 25.4 (s, –CH_2–), 19.3 (s, –CH_2–) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 22.7 (s) ppm.

4.4.4. Preparation of (E)-1-(diphenylphosphinyl)-2-ferrocenylethene (**3**, Table 1, entry 3)

The general procedure was followed using $HP(O)Ph_2$ (0.050 g, 0.25 mmol), ethynylferrocene (0.052 g, 0.25 mmol), and $(PPh_3)_3RhCl$ (0.004 g, 4.3 μmol). After irradiating for 2 min (max power = 25 W, 120 °C), purification of the residue by column chromatography (hexanes/EtOAc) afforded 0.083 g (81%) of the title compound. The identity of

the title compound was established by comparison of the ^{1}H and ^{31}P NMR data with literature values [6].

4.4.5. Preparation of (E)-1-(diphenylphosphinyl)-1-heptene (**4**, Table 1, entry 4)

The general procedure was followed using $HP(O)Ph_2$ (0.050 g, 0.25 mmol), 1-heptyne (32.4 μL, 0.25 mmol), and Rh-bound oligo(vinyl diphenylphosphine-*co*-vinyl diphenylphosphine oxide-*co*-vinyl chloride) (0.008 g). After irradiating for 7 min (max power = 25 W, 120 °C), purification of the residue by column chromatography (hexanes/EtOAc) afforded 0.067 g (91%) of the title compound as a colorless solid. The identity and purity was established by GC as well as ^{1}H and ^{31}P NMR spectroscopy [26].

4.4.6. Preparation of (E)-1-(cyclohexene-1-yl)-2-(diphenylphosphinyl)ethene (**5**, Table 1, entry 5)

The general procedure was followed using $HP(O)Ph_2$ (0.050 g, 0.25 mmol), 1-ethynylcyclohexene (29.1 μL, 0.25 mmol), and Rh-bound supported PPh_3 (0.008 g). After irradiating for 7 min (max power = 25 W, 120 °C), purification of the residue by column chromatography (hexanes/EtOAc) afforded 0.053 g (70%) of the title compound. The identity and purity was established by GC as well as ^{1}H and ^{31}P NMR spectroscopy [6].

4.4.7. Preparation of 1-(4-bromophenyl)-1,2-ethanediyl-bis(diphenylphosphine oxide) (**6**, Table 2, entry 1)

The general procedure was followed using $HP(O)Ph_2$ (0.075 g, 0.37 mmol), 4-ethynylbromobenzene (0.022 g, 0.12 mmol), and $[Rh(cod)Cl]_2$ (0.001 g, 2.0 μmol, 4 μmol Rh). After irradiating for 40 min (max power = 50 W, 120 °C), the residue was washed with ethyl acetate and dried under vacuum affording 0.055 g (76%) of the title compound as a colorless solid. Anal. Calcd. for $C_{32}H_{27}BrO_2P_2$: C, 65.65; H, 4.65. Found: C, 65.40; H, 4.52. ^{1}H NMR ($CDCl_3$, 19 °C): δ 7.99–7.92 (m, 2H, Ar–H), 7.51–7.0 (m, 18H, Ar–H), 6.91–6.82 (m, 4H, Ar–H), 4.18 (m, 1H, –CH– or $–CH_2–$), 3.02 (m, 1H, –CH– or $–CH_2–$), 2.73 (m, 1H, –CH– or $–CH_2–$) ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 19 °C, low-frequency region) δ 38.8 (d, J = 69.3, –CH– or $–CH_2–$), 30.2 (d, J = 69.3, –CH– or $–CH_2–$) ppm. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 19 °C): δ 33.5 (d, J = 46.8, $–P(O)Ph_2$), 28.6 (d, J = 46.8, $–P(O)Ph_2$) ppm.

4.4.8. Preparation of 2-[1,2-bis(diphenylphosphinyl)ethyl]-pyridine (**7**, Table 2, entry 2)

The general procedure was followed using $HP(O)Ph_2$ (0.075 g, 0.37 mmol), 2-ethynylpyridine (12.5 μl, 0.12 mmol), and $[Rh(cod)Cl]_2$ (0.001 g, 2 μmol; 4 μmol Rh). After irradiating the reaction for 40 min (max power = 50 W, 120 °C), the residue was washed with a 1:1 mixture of ethyl acetate/diethyl ether and dried under vacuum affording 0.053 g (84%) of the title compound as a tan solid. The identity was established by comparison of the ^{1}H and ^{31}P NMR data to literature values [20].

4.4.9. Preparation of 1-(4-tolyl)-1,2-ethanediyl-bis(diphenylphosphine oxide) (**8**, Table 2, entry 3)

The general procedure was followed using $HP(O)Ph_2$ (0.075 g, 0.37 mmol), 4-ethynyltoluene (15.7 μl, 0.12 mmol), and $(PPh_3)_3RhCl$ (0.004g, 4.3 μmol). After irradiating the reaction for 40 min (max power = 50 W, 120 °C), the residue was washed with a 1:1 mixture of ethyl acetate/ether and dried under vacuum affording 0.041 g (64%) of the title compound as a colorless solid. Anal. Calcd. for $C_{33}H_{30}O_2P_2$: C, 76.14; H, 5.81. Found: C, 75.60; H, 5.55. ^{1}H NMR ($CDCl_3$): δ 7.99–7.91 (m, 2H, Ar–H), 7.55–6.97 (m, 18H, Ar–H), 6.97 (d, 2H, J = 6.7, Ar–H), 6.60 (d, 2H, J = 7.8, Ar–H), 4.16 (m, 1H, –CH– or $–CH_2–$), 3.07 (m, 1H, –CH– or $–CH_2–$), 2.72 (m, 1H, –CH– or $–CH_2$), 2.00 (s, 3H, $–CH_3$) ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 38.7 (d, J = 66.5, $–PCH–$ or $–PCH_2–$), 30.24 (d, J = 69.4, $–PCH–$ or $–PCH_2–$), 20.8 (s, $–CH_3$) ppm. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 34.0 (d, J = 47.8, $–P(O)Ph_2$), 29.0 (d, J = 47.8, $–P(O)Ph_2$) ppm.

4.4.10. Preparation of 1-cyclohexenyl-1,2-ethanediyl-bis(diphenylphosphine oxide) (**9**, Table 2, entry 4)

The general procedure was followed using $HP(O)Ph_2$ (0.075 g, 0.37 mmol), 1-ethynyl-1-cyclohexene (14.5 μl, 0.12 mmol), and $[Rh(cod)Cl]_2$ (0.001 g, 2 μmol; 4 μmol Rh). After irradiating for 40 min (max power = 50 W, 120 °C), the solid was washed with a 1:1 mixture of ethyl acetate/diethyl ether and dried under vacuum to afford 0.045 g (71%) of the title compound. Anal. Calcd. for $C_{32}H_{32}O_2P_2$: C, 75.28; H, 6.32. Found: C, 74.94; H, 6.24. ^{1}H NMR ($CDCl_3$): δ 7.97 (m, 2H, Ar–H), 7.70 (m, 2H, Ar–H), 7.63–7.50 (m, 7H, Ar–H), 7.45–7.32 (m, 9H, Ar–H), 5.67 (m, 1H, =CH–), 3.61 (m, 1H, –CH– or $–CH_2–$), 3.02 (m, 1H, –CH– or $–CH_2–$), 2.55 (m, 1H, –CH– or $–CH_2–$), 1.83 (m, 1H, $–CH_2–$), 1.63 (m, 1H, $–CH_2–$), 1.42 (m, 1H, $–CH_2–$), 1.13 (m, 1H, $–CH_2–$), 0.88–0.78 (m, 4H, $–CH_2–$) ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$; low-frequency region): δ 39.5 (d, J = 69.4, $–PCH–$ or $–PCH_2–$), 29.0, (s, $–CH_2–$), 27.5 (d, J = 70.3, $–PCH–$ or $–PCH_2–$), 25.2 (s, $–CH_2–$), 22.0 (s, $–CH_2–$), 21.1 (s, $–CH_2–$) ppm. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 33.8 (d, J = 49.7, $–P(O)Ph_2$), 28.7 (d, J = 49.7, $–P(O)Ph_2$) ppm.

4.4.11. Preparation of 3-[1,2-bis(diphenylphosphinyl)ethyl]-pyridine (**10**, Table 2, entry 5)

The general procedure was followed using $HP(O)Ph_2$ (0.075 g, 0.37 mmol), 3-ethynyl pyridine (0.013 g, 0.12 mmol), and $(Ph_3P)_3RhCl$ (0.004 g, 4.3 μmol). After irradiating for 40 min (max power = 50 W, 120 °C), the residue was washed with ethyl acetate and dried under vacuum to afford 0.055 g (88%) of the title compound as a colorless solid. Anal. Calcd. for $C_{31}H_{27}NO_2P_2$: C, 73.37; H, 5.36. Found: C, 73.36; H, 5.43. ^{1}H NMR ($CDCl_3$): δ 8.18 (m, 1H, Ar–H), 8.11–8.02 (m, 3H, Ar–H), 7.61–7.11 (m, 19H,

Ar–H), 6.75 (m, 1H, Ar–H), 4.32 (m, 1H, –CH_2– or –CH–), 3.12 (m, 1H, –CH_2– or –CH–), 2.85 (m, 1H, –CH_2– or –CH–) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, low-frequency region): δ 36.9 (d, J = 105.3, –CH_2– or –CH–), 29.6 (d, J = 105.3, –CH_2– or –CH–) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 34.1 (d, J = 45.4, –P(O)Ph_2), 28.3 (d, J = 45.4, –P(O)Ph_2) ppm.

*4.4.12. Preparation of 1-phenyl-1,2-ethanediyl-bis(diphenylphosphine oxide) (**11**, Table 2, entry 6)*

The general procedure was followed using HP(O)Ph_2 (0.075 g, 0.37 mmol), phenylacetylene (13.6 μL, 0.12 mmol), and Rh-bound oligo(vinyl diphenylphosphine-*co*-vinyl diphenylphosphine oxide-*co*-vinyl chloride) (0.008 g). After irradiating for 40 min (max power = 50 W, 120 °C), the residue was washed with ethyl acetate and died under vacuum affording 0.047 g (75%) of the title compound as a colorless solid. The identity was established by comparison of the ^1H and ^{31}P NMR data to literature values [2].

*4.4.13. Preparation of 1-pentyl-1,2-ethanediyl-bis(diphenylphosphine oxide) (**12**, Table 2, entry 7)*

The general procedure was followed using HP(O)Ph_2 (0.075 g, 0.37 mmol), 1-heptyne (16.2 μL, 0.12 mmol), and Rh-bound supported triphenylphosphine (0.008 g). After irradiating for 40 min (max power = 50 W, 120 °C), the residue was purified by column chromatography (hexanes/EtOAc) affording 0.043 g (70%) of the title compound as a colorless solid. The identity and purity was established by GC as well as ^1H and ^{31}P NMR spectroscopy [26].

*4.4.14. Preparation of (E)-1,2-bis(diphenylphosphinyl)-1-2-butenedioic acid, dimethyl ester (**13**, Table 3, entry 1)*

The general procedure was followed using HP(O)Ph_2 (0.055 g, 0.27 mmol), 1-heptyne (12.5 μL, 0.12 mmol), and $[Rh(cod)Cl]_2$ (0.001 g, 2.0 μmol; 4.0 μmol Rh). After irradiating for 20 min (max power = 50 W, 120 °C), the residue was purified by column chromatography (hexanes/EtOAc) to afford 0.049 g (73%) of the title compound. The identity established by comparison of the ^1H and ^{31}P NMR data to literature values [27].

*4.4.15. Preparation of (E)-1,2-bis(diphenylphosphinyl)-1-2-butenedioic acid, dimethyl ester without catalyst (**13**, Table 3, entry 2)*

The general procedure was followed using new glassware and a new stirring bar. A round-bottomed flask was charged with HP(O)Ph_2 (0.055 g, 0.27 mmol) and DMAD (12.5 μL, 0.12 mmol). After irradiating for 20 min (max power = 50 W, 120 °C), the residue was purified by column chromatography (hexanes/EtOAc) to afford 0.043 g (64%) of the title compound. The identity and purity was established by GC as well as ^1H and ^{31}P NMR spectroscopy.

*4.4.16. Preparation of (E)-1,2-bis(diphenylphosphinyl)-1-diphenyl acetylene (**14**, Table 3, entry 3)*

The general procedure was followed using HP(O)Ph_2 (0.055 g, 0.27 mmol), diphenylacetylene (0.044 g, 0.25 mmol), and $(Ph_3P)_3RhCl$ (0.004 g, 4.3 μmol). After irradiating for 20 min (max power = 50 W, 120 °C), purification of the residue by column chromatography (hexanes/EtOAc) afforded 0.052 g (55%) of the title compound as a colorless solid. The identity and purity was established by GC as well as ^1H and ^{31}P NMR spectroscopy [28].

4.4.17. Treatment of HP(O)Ph_2 with diphenylacetylene without catalyst (Table 3, entry 4)

The general procedure was followed using new glassware and a new stirring bar. The microwave reactor vial was charged with HP(O)Ph_2 (0.055 g, 0.27 mmol), and diphenylacetylene (0.044 g, 0.25 mmol). After irradiating for 20 min (max power = 50 W, 120 °C), analysis by ^1H and ^{31}P NMR spectroscopy revealed only the starting materials.

*4.4.18. Preparation of (E)-1,2-bis(diphenylphosphinyl)-4-octyne (**15**, Table 3, entry 5)*

The general procedure was followed using HP(O)Ph_2 (0.05 g, 0.25 mmol), 4-octyne (18.1 μL, 0.12 mmol), and Rh-bound oligo(vinyl diphenylphosphine-*co*-vinyl diphenylphosphine oxide-*co*-vinyl chloride) (0.008 g). After irradiating for 20 min (max power = 50 W, 120 °C), purification of the residue by column chromatography (hexanes/EtOAc) afforded 0.043 g (62%) of the title compound. The identity of the title compound was confirmed by comparison of the ^1H and $^{31}P\{^1H\}$ NMR data with literature values [6].

4.4.19. Treatment of HP(O)Ph_2 with 4-octyne without catalyst (Table 3, entry 6)

The general procedure was followed using new glassware and a new stirring bar. The microwave reactor vial was charged with HP(O)Ph_2 (0.055 g, 0.27 mmol), and 4-octyne (18.1 μL, 0.25 mmol). After irradiating for 20 min (max power = 50 W, 120 °C), analysis by ^1H and ^{31}P NMR spectroscopy revealed only the starting materials.

4.5. Conventional heating with solid-supported catalysts

A screw-cap vial was charged with diphenylphosphine oxide (0.100 g, 0.50 mmol) and catalyst (0.016 g). After sealing with a septum, evacuating, and refilling with nitrogen, the alkyne (0.50 mmol) and toluene (2 mL) were added. When solid alkynes were used, they were added prior to evacuation. The septum was replaced by a screw-cap (in the glove-box) and the reaction was stirred for 4 h at 75 °C. The toluene was removed under vacuum and the residue was purified by column chromatography. The identity of the alkenylphosphine oxides was established by GC–MS and a comparison of the ^1H and ^{31}P NMR data to literature values [6].

Acknowledgements

This work was supported by a New Faculty Award from the Henry and Camille Dreyfus Foundation (Award-SU-00-020).

Thanks are given to Elaine D. Keithan for help in obtaining the trace ICP-AES data.

References

[1] P. Rey, J. Taillades, J.C. Rossi, G. Gros, Tetrahedron Lett. 44 (2003) 6169.
[2] D. Semenzin, G. Etemad-Moghadam, D. Albouy, O. Diallo, M. Koenig, J. Org. Chem. 62 (1997) 2414.
[3] F. Alonso, I.P. Beletskaya, M. Yus, Chem. Rev. 104 (2004) 3079.
[4] D.K. Wicht, I.V. Kourkine, B.M. Lew, J.M. Nthenge, D.S. Glueck, J. Am. Chem. Soc. 119 (1997) 5039.
[5] P.G. Pringle, M.B. Smith, J. Chem. Soc., Chem. Commun. (1990) 1701.
[6] L.B. Han, C.Q. Zhao, M. Tanaka, J. Org. Chem. 66 (2001) 5929.
[7] L.B. Han, F. Mirzaei, C.Q. Zhao, M. Tanaka, J. Am. Chem. Soc. 122 (2000) 5407.
[8] S. Deprele, J.L. Montchamp, J. Am. Chem. Soc. 124 (2002) 9386.
[9] M. Larhed, C. Moberg, A. Hallberg, Acc. Chem. Res. 35 (2002) 717.
[10] P. Lidstrom, J. Tierney, B. Wathey, J. Westman, Tetrahedron 57 (2001) 9225.
[11] P. Nilsson, H. Gold, M. Larhed, A. Hallberg, Synthesis 11 (2002) 1611.
[12] B. Basu, P. Das, M.M.H. Bhuiyan, S. Jha, Tetrahedron Lett. 44 (2003) 3817.
[13] P. Walla, C.O. Kappe, Chem. Commun. (2004) 564.
[14] D.K. Rohrbaugh, F.R. Longo, H.D. Durst, S. Munavalli, Phosphorus, Sulfur, Silicon Relat. Elem. 176 (2001) 201.
[15] B.M. Trost, Acc. Chem. Res. 35 (2002) 695.
[16] T.J. Dickerson, N.N. Reed, K.D. Janda, Chem. Rev. 102 (2002) 3325.
[17] Q.H. Fan, Y.M. Li, A.S.C. Chan, Chem. Rev. 102 (2002) 3385.
[18] C.E. Song, S.G. Lee, Chem. Rev. 102 (2002) 3495.
[19] C. Ogawa, H. Konishi, M. Sugiura, S. Kobayashi, Org. Biomol. Chem. 2 (2004) 446.
[20] A. Allen, L. Ma, W.B. Lin, Tetrahedron Lett. 43 (2002) 3707.
[21] A.F. Borowski, Transition Met. Chem. 8 (1983) 266.
[22] D.M. Roundhill, R.P. Sperline, W.B. Beaulieu, Coord. Chem. Rev. 26 (1978) 263.
[23] P. Terreros, E. Pastor, J.L.G. Fierro, J. Mol. Catal. 53 (1989) 359.
[24] N.P. Allen, R.P. Burns, J. Dwyer, C.A. McAuliffe, J. Mol. Catal. 3 (1978) 325.
[25] G.Q. Li, R. Govind, Inorg. Chim. Acta 230 (1995) 219.
[26] L.A. Solovetskaya, N.M. Sergeev, R.K. Magdeeva, E.E. Nifant'ev, Zh. Obshch. Khim. 55 (1985) 1201.
[27] E. Fluck, W. Kazenwadel, Phosphorus Relat. Group V Elem. 6 (1976) 195.
[28] L.B. Han, N. Choi, M. Tanaka, Organometallics 15 (1996) 3259.