ChemInform Abstract: Unprecedented Control of Selectivity in Nickel-Catalyzed Hydrophosphorylation of Alkynes: Efficient Route to Mono- and Bisphosphonates.

ARTICLE *in* ADVANCED SYNTHESIS & CATALYSIS · SEPTEMBER 2014

Impact Factor: 5.66 · DOI: 10.1002/adsc.201400123

Advanced Synthesis & Catalysis

DOI: 10.1002/adsc.201400123

Unprecedented Control of Selectivity in Nickel-Catalyzed Hydrophosphorylation of Alkynes: Efficient Route to Mono- and Bisphosphonates

Levon L. Khemchyan,[a] Julia V. Ivanova,[a] Sergey S. Zalesskiy,[a] Valentine P. Ananikov,[a,*] Irina P. Beletskaya,[b] and Zoya A. Starikova[c]

[a] Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Leninsky Prospect 47, Moscow, 119991, Russia
Fax: (+7)-499-135-5328; e-mail: val@ioc.ac.ru
[b] Chemistry Department, Lomonosov Moscow State University, Vorob′evy gory, Moscow, 119899, Russia
[c] Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Vavilova str. 28, Moscow, 119991, Russia

Received: February 3, 2014; Published online: March 3, 2014

Dedicated to the memory of Z. A. Starikova.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201400123.

Abstract: A unique nickel-based catalytic system was developed where the direction of the hydrophosphorylation reaction can be controlled by varying the catalyst loading. A flexible one-pot access to vinylmonophosphonates and alkylbisphosphonates was demonstrated using simple starting materials in an atom-economic reaction without any specific solvents or ligands. Monitoring of the reaction mechanism with joint NMR and MS studies revealed key information about the reaction intermediates. The synthetic scope of the developed catalytic system was explored and the utility of the synthesized products for the fire protection of cotton materials was demonstrated.

Keywords: alkynes; homogeneous catalysis; nickel; phosphorylation; selectivity

Introduction

Mono- and bisphosphonates are proven as well-suited building blocks for plenty of applications in various fields. Monophosphonates serve as monomers,[1] environmentally-friendly halogen-free flame retardants,[2] versatile building blocks in organic synthesis,[3] and demanding materials for a large number of medical applications.[4] For instance, α-arylvinylphosphonates were successfully used for the synthesis of drug analogues such as Naproxen, Ibuprofen, and Fosmidomycin.[5] Vinylphosphonates can be used as simple and convenient precursors of 3,4-substituted derivatives of (2*S*)-2-amino-4-phosphonobutanoic acid (L-AP4).[6] L-AP4 is a well-known drug with recognized and promising potential to treat central nervous system diseases (including Parkinson's and Alzheimer's diseases).[7] Variations in the nature of the substituents in the starting vinylphosphonate allow the preparation of L-AP4 derivatives with desirable structural and medical properties.

Bisphosphonates are valuable phosphoro-organic compounds with a number of derivatives being utilized as drugs against bone, dental, and other diseases (including osteoporosis and Paget's disease).[8] Due to the capability for metal chelation, the bisphosphonates play a significant role as complexing agents.[9] The initial non-medical applications of bisphosphonates pertain to the oil industry[10] with potential interest for the future development.[11]

New fire safety standards have enforced a re-thinking the concept of flame retardants and demanded novel organophosphonate derivatives.[12] Efficient synthetic strategies are required to access a variety of compounds with different substituents to fulfill requirements in the area of fire protection.

A number of vinylphosphonates is available *via* catalytic hydrophosphorylation of alkynes (addition of H-phosphonates to the carbon-carbon triple bond). Numerous findings in this area were reported and the subject was discussed in numerous reviews.[13] The vast majority of the reactions utilized palladium com-

plexes as catalysts,[5a,b,14] however several examples of Rh- and Ni-catalyzed reactions were also reported.[15]

Unfortunately the existing methods of alkyne hydrophosphorylation have some drawbacks that are often crucial for practical applications, particularly the use of expensive (Rh, Pd) or unstable [$Ni(COD)_2$] metal catalysts, predominant use of phosphine ligands and organic solvents which results in the formation of toxic wastes. Moreover, to the best of our knowledge, there is only one example describing the synthesis of bisphosphonates *via* the double hydrophosphorylation of terminal alkynes [5 mol% of $Pd(PPh_3)_4$ as a catalyst, suitable only for a limited range of alkynes].[16,17] Besides the limited scope of substrates, another common drawback of known synthetic procedures is low reaction selectivity leading to the formation of mixtures of mono- and bisphosphonates. Finally, examples of catalytic double hydrophosphorylation of internal alkynes have not been reported up to date.

Herein we report a new and efficient catalytic system which is not affected by the shortcomings listed above. We employed inexpensive commercially available $Ni(acac)_2$ as catalyst precursor.

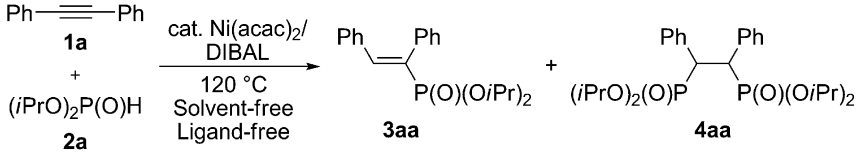
Results and Discussion

The hydrophosphorylation of diphenylacetylene **1a** with $(i\text{-PrO})_2P(O)H$ **2a** was chosen as the model reaction (Table 1). The reaction does not proceed upon heating of the mixture of **1a**, **2a** and $Ni(acac)_2$. However, we have found that addition of a catalytic amount of diisobutylaluminum hydride (DIBAL) allows us to reach 100% conversion of starting materials **1a** and **2a**. Indeed, the use of the $Ni(acac)_2$ (9 mol%)/DIBAL system led to the desired *syn*-addition product **3aa** with 99% yield and complete stereoselectivity (Table 1, entry 1). Remarkably, no solvent, ligand or any other additive was required to reach the complete conversion of **2a** into **3aa** in only 40 min. To prove the catalytic effect we conducted the same reaction in the absence of $Ni(acac)_2$. Without the catalyst only traces (2–3%) of **4aa** were detected by $^{31}P\{^1H\}$ NMR.

An unusual finding was the dependence of the product yield and composition on the catalyst loading (Table 1, entries 1–3). Utilization of 4.5 and 2 mol% of Ni decreased the yield of **3aa** to 86 and 47%, respectively, while the conversion of H-phosphonate **2a** was kept at 100%. An analysis of the $^{31}P\{^1H\}$ NMR spectra of the reaction mixtures revealed the formation of bisphosphonate **4aa** as reaction product together with **3aa** (Table 1, entries 2 and 3). The yield of **4aa** was higher at decreased loadings of $Ni(acac)_2$. Indeed, as little as 1 mol% of Ni catalyst led to a 63% yield of **4aa** after 3.5 h (Table 1, entry 4). Eventually, application of 1 mol% of $Ni(acac)_2$ and optimization of the reaction conditions (reaction time and **1a**:**2a** ratio) allowed us to reach a quantitative yield of bisphosphonate **4aa** without traces of **3aa** or other side-products (Table 1, entry 5). Thereby, the selective synthesis of either **3aa** or **4aa** was found to be possible by a simple change of the nickel catalyst loading and the **1a**:**2a** ratio.

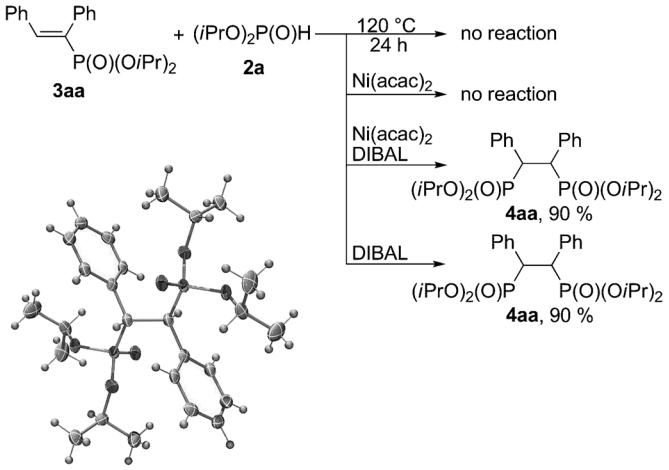
The unprecedented catalytic switch discovered in the present study is superior to tune the direction of the addition reaction. Due to the absence of ligands, solvent or additives the synthesized monophosphonate **3aa** and bisphosphonate **4aa** could be easily isolated from the crude reaction mixture. As expected, **4aa** represented a composition of racemate and *meso*-form which were successfully separated by means of dry column chromatography. The structure of ***meso*-4aa** was confirmed with the combination of 1D, 2D NMR experiments and X-ray analysis. ^1H-^{31}P HMBC, ^1H-^{13}C HSQC and ^1H-^{13}C HMBC experiments were used to establish the structure of ***rac*-4aa**, the measured chemical shifts and coupling con-

Table 1. The model hydrophosphorylation of **1a** with **2a**: dependence of selectivity on $Ni(acac)_2$ loadings.[a]



Entry	$Ni(acac)_2$ [mol%]	Conditions (time and **1a**:**2a** molar ratio)	Yield of **3aa**[b] [%]	Yield of **4aa**[b,c] [%]
1	9	40 min (1:1)	99	0
2	4.5	1 h (1:1)	86	13
3	2	1 h (1:1)	47	52
4	1	3.5 h (1:1)	36	63
5	1	28 h (1:2.5)	0	99

[a] 2 equiv. of DIBAL relative to $Ni(acac)_2$ were used, see the Experimental Section for details.
[b] Determined by $^{31}P\{^1H\}$ NMR. In the cases of entries 1–4 the yields are given based on the initial amount of H-phosphonate **2a**; in the case of entry 5 the yield is given based on the initial amount of alkyne **1a**.
[c] **4aa** represents a mixture of *rac*- and *meso*-forms.



X-ray structure of *meso*-**4aa**

Scheme 1. Hydrophosphorylation of **3aa** with **2a** [4.5 mol% of $Ni(acac)_2$ and 9 mol% of DIBAL; see the Experimental Section for details].

stants were in agreement with literature data for similar phosphorus-containing molecules.[18]

Formation of bisphosphonate **4aa** is a one-pot process which proceeds *via* subsequent hydrophosphorylation of vinylphosphonate **3aa** with a second molecule of **2a**. To explore this step, four independent experiments were conducted (Scheme 1). Freshly synthesized and purified **3aa** was used as the starting material for the reaction with **2a**. Good yields of **4aa** were reached in the presence of the $Ni(acac)_2$/DIBAL or DIBAL alone. Thus, it can be proposed that the transformation of monophosphonate to bisphosphonate was mediated by a catalytic amount of DIBAL.

The observed dependence of reaction selectivity on $Ni(acac)_2$ loading (Table 1) may be explained by the following factors. At higher $Ni(acac)_2$ loading the H-phosphonate **2a** is rapidly converted into **3aa**. Indeed, $^{31}P\{^1H\}$ NMR monitoring of the reaction with **1a**:**2a** = 1:1 molar ratio revealed that the use of 9 mol% of $Ni(acac)_2$ (Table 1, entry 1) leads to approximately 80% of **2a** being consumed in 5 min with **3aa** being the only product. Lowering the catalyst loading (while retaining the 1:1 phosphonate to alkyne molar ratio) leads to decrease in **3aa** formation rate making it possible for the H-phosphonate **2a** to react with *in situ* formed **3aa** leading to bisphosphorylation adduct **4aa**. To achieve quantitative yield of **4aa** the excess of H-phosphonate to alkyne was used (Table 1, entry 5).

Furthermore, we examined the performance of different nickel catalyst precursors in the model reaction (Table 2). The use of $NiBr_2$ and $NiCl_2$ showed good results comparable to those for $Ni(acac)_2$ and the selectivity was slightly better (Table 2, *cf.* entries 1, 2 and 3). However, among the studied Ni(II) catalyst precursors, $Ni(acac)_2$ is preferable to design a halogen-free catalytic system.

Table 2. The model hydrophosphorylation of **1a** with **2a**: evaluation of performance of different Ni catalyst precursors.[a]

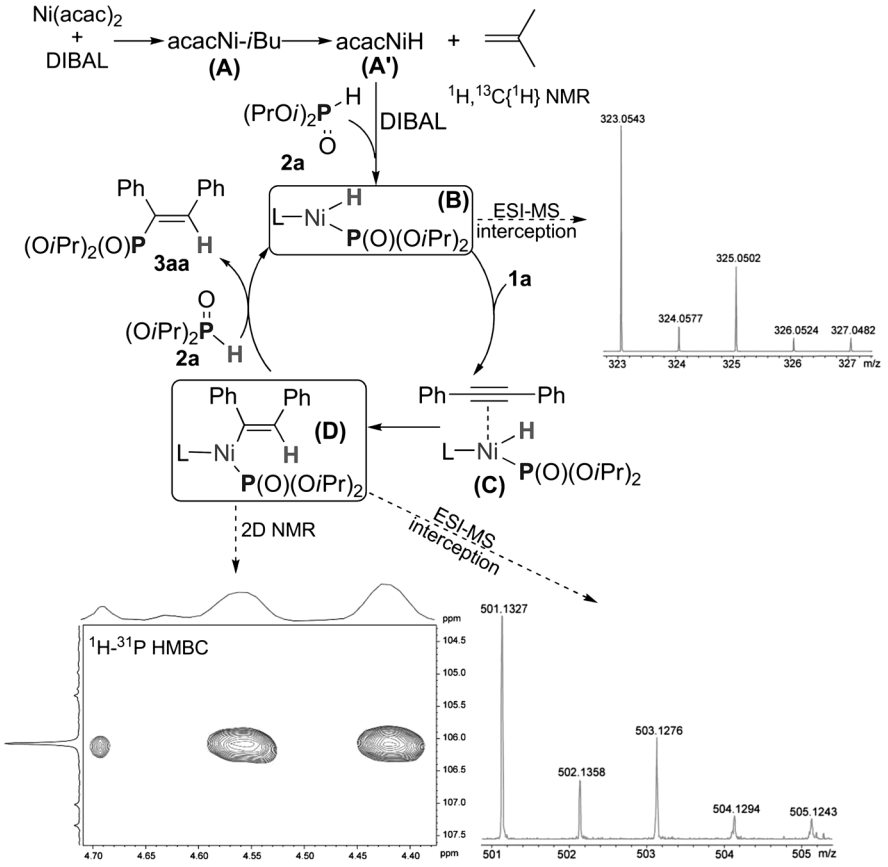
Entry	Catalyst precursor	Yield **3aa**/**4aa**[b] [%]	
		With DIBAL	Without DIBAL
1	$Ni(acac)_2$	86/13	0/0
2	$NiBr_2$	93/3	0/0
3	$NiCl_2$	87/3	0/0
4	$Ni(COD)_2$	53/46	9/0[c]

[a] **1a** (1 mmol), **2a** (1 mmol), [Ni] (4.5 mol%), DIBAL (9 mol%), 120 °C, 3 h; see the Experimental Section for additional details.
[b] Determined by $^{31}P\{^1H\}$ NMR.
[c] 9 mol% of $Ni(COD)_2$, 120 °C, 19 h.

The case of $Ni(COD)_2$ deserves special attention. It is well-known that $Ni(COD)_2$ is a highly reactive compound due to the presence of the Ni(0) center and labile cyclooctadiene ligands. However, in our case only a trace amount of product **3aa** was formed in the absence of DIBAL (Table 2, entry 4). It is evident that Ni(0) itself does not govern the catalytic cycle. This means that in the $Ni(acac)_2$/DIBAL system the latter component serves not only to reduce Ni(II) to Ni(0), but also to promote the formation of Ni-containing catalytically active species. It is known that reduction of Ni(II) upon interaction of $Ni(acac)_2$ with DIBAL proceeds *via* formation of acacNi-*i*-Bu species (**A**) (Scheme 2).[19] Further β-hydride elimination leads to formation of active nickel hydride acacNiH (**A′**) and isobutylene (detected in our study by *in situ* ^1H and ^{13}C NMR). On the next step interaction with H-phosphonate molecule yields complex **B** which enters the catalytic cycle (Scheme 2 and discussion below).

It should be noted that the initial presence of H-phosphonate **2a** in the catalytic system was essential for the activation of catalyst precursor and to avoid degradation of *in situ* formed active hydride species. This fact was proven by the additional experiment with the reversed order of reagent addition: **1a** and **2a** were placed in the reaction vessel after mixing of $Ni(acac)_2$ and DIBAL [normally, DIBAL was added to the mixture of **1a**, **2a** and $Ni(acac)_2$]. Indeed, only 48% conversion of **2a** was observed [9 mol% of $Ni(acac)_2$, 1 h].[20] It is known that **2a** exists in equilibrium with its tautomeric form $(i\text{-PrO})_2$P-OH[21] which has a lone electron pair on the phosphorus atom. Thus, the H-phosphonate can also act as a ligand to stabilize the species **B** and **D**.[22]

To get insight into the mechanistic picture we performed combined NMR and ESI-MS monitoring of the hydrophosphorylation reaction.[20] The use of both NMR and MS allowed a number of Ni-containing complexes to be independently detected (see the Sup-



Scheme 2. Plausible catalytic cycle for the hydrophosphorylation reaction based on ESI-MS and NMR monitoring.[20]

porting Information, Figures S1, S2, and S3). The interaction of **A′** with **2a** leads to the formation of intermediate **B** which was intercepted by ESI-MS (Scheme 2, Figure S1). The next step involves the formation of complex **C** *via* coordination of alkyne **1a** to the Ni atom of complex **B**. Subsequent insertion of the alkyne into the Ni–H bond in **C** results in formation of vinyl complex **D**, which was successfully intercepted by ESI-MS (Scheme 2, Figure S1) and independently detected by NMR ($^{31}P\{^{1}H\}$ chemical shift: 106.2 ppm; Figures S2 and S3).[20] The observed formation of complex **D** is in agreement with theoretical calculations, where it was shown that alkyne insertion into the metal-hydrogen bond is much more favorable compared to alkyne insertion into the metal-phosphorus bond.[23] Further reductive elimination of product **3aa** from complex **D** leads to regeneration of **B** after reaction with **2a**.

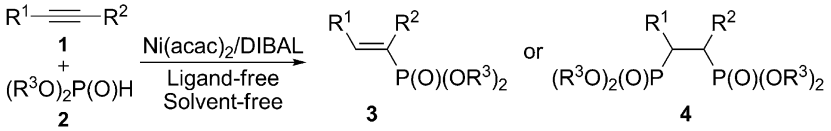
Subsequently we tested the application of the developed $Ni(acac)_2$/DIBAL catalytic system towards the synthesis of different mono- and bisphosphonates (Table 3). The corresponding products **3** and **4** were obtained with excellent yields both for symmetrical internal alkyne **1a** (Table 3, entries 1 and 2) and for unsymmetrical internal alkyne **1b** (Table 3, entries 3 and 4).

The developed catalytic procedure demonstrated high yields of bisphosphonates formed from alkynes **1c**–**1e** at high and low Ni loadings (Table 3, entries 5–10). In case of internal alkyne **1f** the monophosphonate **3fa** was selectively formed with 90% yield with 9 mol% of $Ni(acac)_2$, however only 19% of **3fa** was formed when 1 mol% of $Ni(acac)_2$ was taken (Table 3, entries 11 and 12). Various other bis- and monophosphonates were prepared in good to high yields using our catalytic system (Table 3, entries 13–17).

Although nickel complexes are known to promote alkyne polymerization,[24] in the present case this side reaction did not make a significant contribution, thus having no impact on the performance of the synthetic procedure. Furthermore, the developed catalytic system was tolerant to the steric bulkiness of R^3 substituents (i-C_3H_7, C_6H_5, $C_{12}H_{25}$) in compound **2**, allowing a number of corresponding products to be successfully synthesized (Table 3).

Finally, we studied the efficiency of the synthesized compounds as potential flame protection materials. The specimens of cotton textile (control sample and

Table 3. The scope of the Ni-catalyzed hydrophosphorylation of alkynes.[a]



1a: R^1=R^2=Ph; **1b**: R^1=Ph, R^2=Me; **2a**: R^3=*i*Pr
1c: R^1=Ph, R^2=H; **1d**: R^1=C_5H_{11}, R^2=H; **2b**: R^3=Ph
1e: R^1=Me_3Si, R^2=H; **1f**: R^1=R^2=Et; **2c**: R^3=$C_{12}H_{25}$

Entry	Alkyne	H-phosphonate	Ni (mol%)	Yield[b] [%]	Product
1	**1a**	**2a**	9	99	**3aa**
2	**1a**	**2a**	1	99	**4aa**
3	**1b**	**2a**	9	90	**3ba**
4	**1b**	**2a**	1	75	**4ba**
5	**1c**	**2a**	9	97	**4ca**
6	**1c**	**2a**	1	80	**4ca**
7	**1d**	**2a**	9	99	**4da**
8	**1d**	**2a**	1	72	**4da**
9	**1e**	**2a**	9	85	**4ea**
10	**1e**	**2a**	1	80	**4ea**
11	**1f**	**2a**	9	90	**3fa**
12	**1f**	**2a**	1	19	**3fa**
13	**1a**	**2b**	9	95	**3ab**
14	**1b**	**2b**	9	60	**3bb**
15	**1a**	**2c**	4.5	95	**3ac**
16	**1b**	**2c**	4.5	77	**3bc**
17	**1d**	**2b**	9	95	**4db**

[a] See the Experimental Section and Supporting Information for details.
[b] Determined by $^{31}P\{^1H\}$ NMR. In the cases of entries 1, 3, 5–17 the yields are given based on the initial amount of H-phosphonate **2**; in the case of entries 2 and 4the yields are given based on the initial amount of alkyne **1a**.

two samples impregnated with solutions of **3aa** and *meso*-**4aa**) were investigated by field-emission scanning electron microscopy (FE-SEM) after combustion. The study demonstrated a high impact of the pretreatment of cotton textile on their flame resistivity (Figure 1).

FE-SEM showed that the native textile consisted of the regular structure with the mean fiber diameter of about 14 μm (Figure 1A). After combustion of the textile the structure had dramatically changed. The average fiber diameter was lowered down to 4 μm resulting in formation of a deformed structure (Figure 1B). For the samples pretreated with **3aa** and *meso*-**4aa** FE-SEM revealed negligible changes in the general morphology after combustion (Figure 1C and D). The fine structure of the fibers had no cracks, spikes and the fibers possessed a smooth surface. Apparently, compounds **3aa** and *meso*-**4aa** protected cotton fibers from structural distortions. In the case of **3aa** the mean fiber diameter was about 13 μm and in the case of *meso*-**4aa** about 14 μm. Thus, both compounds showed good efficiency as potential fire protection materials. In fact, no critical deformations were observed on comparing native non-burned textile and pretreated samples after burning (*cf.* Figure 1A and C, D). The product of double phosphorylation reaction showed slightly better protection properties (the larger thickness of individual fibers was preserved after burning; Figure 1D). However, this is a preliminary observation only that needs to be further studied in more detail.

Conclusions

In summary, the superior performance of the $Ni(acac)_2$/DIBAL system in catalytic hydrophosphorylation of alkynes was revealed. Remarkably, no specific solvents or ligands were required to reach complete conversion of the starting materials into the desired products. The unique selectivity switch discovered in the present study made it possible to direct the reaction in the desired way by a simple change of the catalyst loading and reagent ratio. The formation of either mono- or bisphosphonates can be achieved with the developed system.

The inexpensive, halogen-free and easy to handle catalyst precursor $Ni(acac)_2$ makes the synthetic procedure convenient for practical usage. The catalytic system developed provides a cost-efficient and green

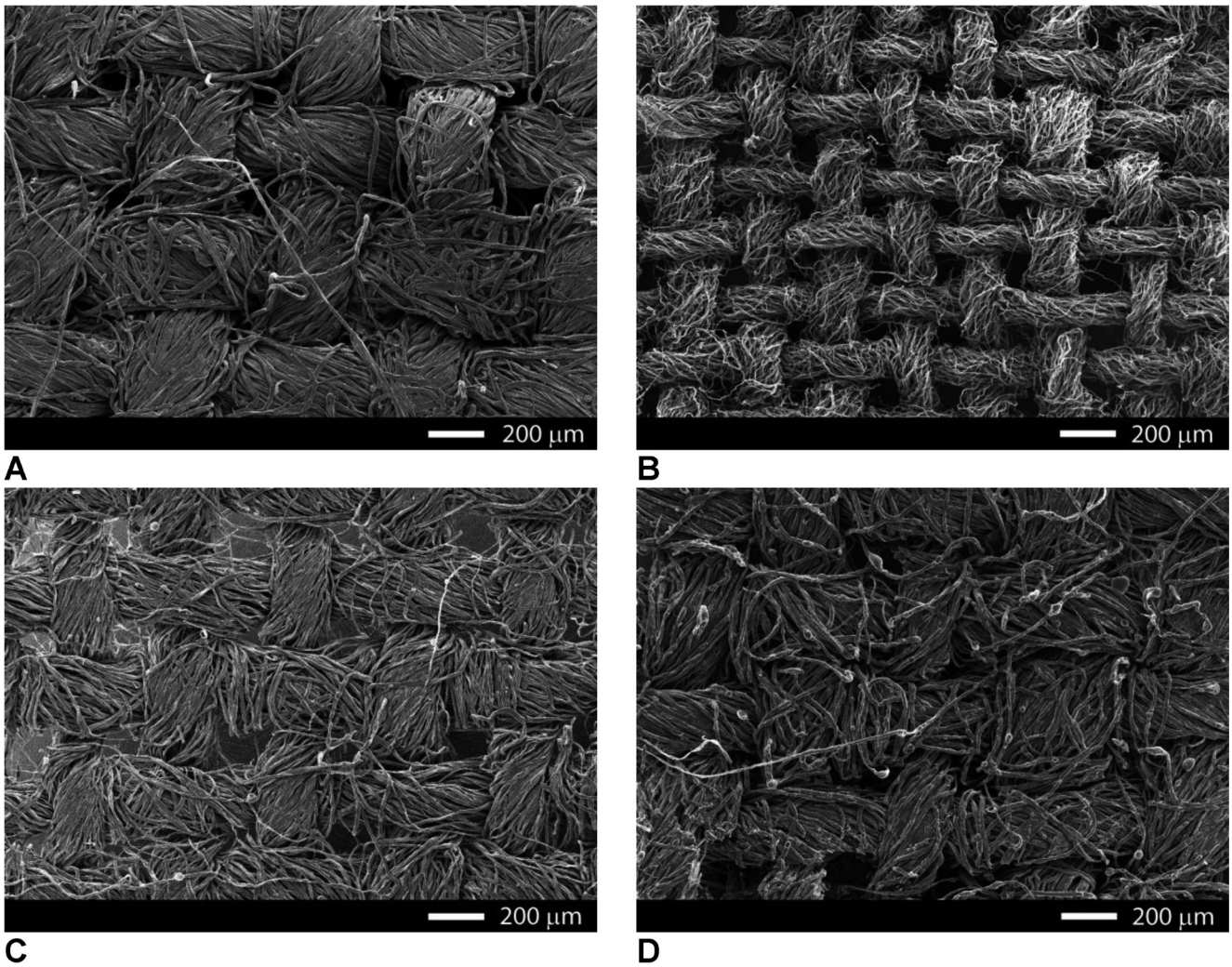


Figure 1. FE-SEM images of the cotton textile: native material before burning (A), after burning without pretreatment (B), after pretreatment with **3aa** and *meso*-**4aa** followed by burning (C and D, respectively).

chemical method to create C–P bonds. Demanding fire-protective phosphonate derivatives were prepared in one-pot procedures from readily available starting compounds.

Experimental Section

General Synthetic Procedure (Table 1)

Conditions *i* (for entries 1–4): **1a** (1.0 mmol, 178.2 mg), **2a** (1.0 mmol, 0.167 mL), and $Ni(acac)_2$ were placed into a reaction vessel and stirred at room temperature for 5 min. DIBAL (1 M solution in THF) was added to the obtained green mixture under stirring and a continuous flow of argon. The color of the mixture immediately turned from green to black. The reaction was carried out at 120 °C under stirring. See Table 1 for reaction times. Molar ratio $Ni(acac)_2$/DIBAL was 1/2 for all reactions. The used quantities of $Ni(acac)_2$ were 9×10^{-2} mmol (23.1 mg) (entry 1); 4.5×10^{-2} mmol (11.6 mg) (entry 2); 2.0×10^{-2} mmol (5.1 mg) (entry 3); 1.0×10^{-2} mmol (2.6 mg) (entry 4). The used quantities of DIBAL (1 M solution in THF) were 18×10^{-2} mmol (0.18 mL) (entry 1); 9×10^{-2} mmol (0.09 mL) (entry 2); 4×10^{-2} mmol (0.04 mL) (entry 3); 2×10^{-2} mmol (0.02 mL) (entry 4).

Conditions *ii* (for entry 5): **1a** (1.0 mmol, 178.2 mg), **2a** (1.0 mmol, 0.167 mL), and $Ni(acac)_2$ (1.0×10^{-2} mmol, 2.6 mg) were placed into a reaction vessel and stirred at room temperature for 5 min. DIBAL (1 M solution in THF, 2×10^{-2} mmol, 0.02 mL) was added to the obtained green mixture under stirring and a continuous flow of argon. The color of the mixture immediately turned from green to black. The reaction was carried out at 120 °C under stirring. After 4 h the heating was stopped and **2a** (1.5 mmol, 0.250 mL), DIBAL (1 M solution in THF, 2×10^{-2} mmol, 0.02 mL) were added to the reaction mixture under a continuous flow of argon. The heating was continued at the same temperature for 24 h under stirring.

Hydrophosphorylation of 3aa with 2a (Scheme 1)

The **conditions *i*** of the general synthetic procedure as described above were used. **3aa** (1.0 mmol, 344.2 mg) was taken as starting material. Molar ratio **3aa**/**2a** was 1/1 (the used quantities: 344.2 mg of **3aa**, 0.167 mL of **2a**) for all reactions except the reaction where the $Ni(acac)_2$/DIBAL catalytic system was utilized. In the latter case a 1/1.5 molar ratio of **3aa**/**2a** was used (the used quantities: 344.2 mg of **3aa**, 0.250 mL of **2a**). See Scheme 1 for more details.

Evaluation of Performance of Different Ni Catalyst Precursors (Table 2)

1a (1.0 mmol, 178.2 mg), **2a** (1.0 mmol, 0.167 mL), and Ni catalyst precursor (4.5×10^{-2} mmol) were placed into a reaction vessel and stirred at room temperature for 5 min. DIBAL (1 M solution in THF, 9×10^{-2} mmol, 0.09 mL) was added to the obtained mixture under stirring and a continuous flow of argon. The reaction was carried out at 120 °C for 3 h under stirring.

NMR Experiments

All NMR measurements were performed with Bruker DRX 500 and Avance 600 spectrometers operating at 500.1 and 600.1 MHz for ^{1}H, 202.5 and 242.9 MHz for ^{31}P and 125.8 and 150.9 MHz for ^{13}C nuclei. Unless otherwise noted, the samples for NMR experiments were prepared directly after the end of heating. The ^{1}H NMR chemical shifts are reported relative to TMS as internal standard. The ^{13}C NMR chemical shifts are reported relative to the corresponding deuterated solvent signals used as internal reference. The ^{31}P NMR chemical shifts are reported relative to external standard H_3PO_4/H_2O. The spectra were processed with the Bruker Topspin 2.1 software package.

ESI-MS Experiments

The samples for ESI-MS analysis of the isolated pure products **3** and **4** were prepared in 1.5 mL Eppendorf tubes (MeCN solutions). All plastic disposables (Eppendorf tubes and tips) used in sample preparation were washed with MeCN before use.

The samples for mechanistic ESI-MS investigation of the hydrophosphorylation reaction (see also the Supporting Information) were prepared by taking an aliquot of the reaction mixture under an argon atmosphere using a glass syringe. The aliquot was then immediately diluted with MeCN directly in the syringe and injected into the ion source of the mass spectrometer.

ESI-mass spectra were recorded on a high resolution Bruker maXis instrument equipped with an electrospray ionization (ESI) ion source. The measurements were performed in a positive (+MS) ion mode (interface capillary voltage: 4500 V) with scan range m/z: 50–3000. External calibration of the mass spectrometer was performed with Electrospray Calibrant Solution (Fluka). A direct syringe injection was used for all the analyzed solutions in MeCN (flow rate: 3 μL min^{-1}). Nitrogen was used as nebulizer gas (0.4 bar) and dry gas (4.0 L min^{-1}); interface temperature was set at 180 °C. Recorded spectra were processed using the Bruker DataAnalysis 4.0 software package.

FE-SEM Experiments

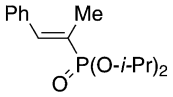
For the FE-SEM measurements samples were mounted on a 25 mm aluminum specimen stub and fixed by conductive silver paint. The observations were carried out using a Hitachi SU8000 field-emission scanning electron microscope (FE-SEM). Images were acquired in secondary electron mode at 10 kV accelerating voltage and at the working distance of 8–10 mm. For the sample of native cotton textile, metal coating with a thin film (10 nm) of Pt/Pd alloy (80/20) was performed using the magnetron sputtering method as described earlier.[25] The morphology of the coated samples was studied as adjusted for the metal coating surface effects.

For burning experiments (Figure 1C, D) cotton material was treated with a solution of vinylphosphonate **3aa** (50 mg) or 1,2-bisphosphonate *meso*-**4aa** (50 mg) in dichloromethane (1 mL) at room temperature for two minutes. Then the material was dried at 50 °C for 10 min. All samples were kept under standard atmospheric pressure for at least 24 h prior to experiments.

Purification and Characterization of Products

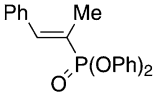
After completion of the reaction the products were purified by dry column vacuum chromatography on silica.[26] Hexanes/ethyl acetate/ethanol gradient elution was applied. After evaporation of solvents under vacuum the pure products were obtained. Dry column flash chromatography has several practical advantages: 1) only a small amount of silica required, 2) quick elution, and 3) economy of solvents. However, slightly better isolated yields (by 5–10%) may be achieved using conventional column chromatography.

Diisopropyl [(*E*)-1-methyl-2-phenylvinyl]phosphonate (3ba): Yellow oil; yield; 200 mg (71%). ^{1}H NMR



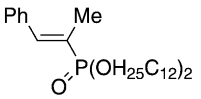
(500.1 MHz, $CDCl_3$, 25 °C, TMS): $\delta=7.48$ [d, $^3J(P,H)_{cis}=24.9$ Hz, 1H], 7.42–7.34 (m, 4H), 7.34–7.26 (m, 1H), 4.77–4.66 (m, 2H), 2.07 [d, $^3J(P,H)=15.2$ Hz, 3H], 1.38 [d, $J(H,H)=6.2$ Hz, 6H], 1.32 [d, $J(H,H)=6.2$ Hz, 6H]; ^{13}C NMR (125 MHz, $CDCl_3$): $\delta=141.96$ [$^2J(P,C)=11.9$ Hz], 136.11 [$^3J(P,C)=23.8$ Hz], 129.53, 128.47, 128.30, 127.60 [$^1J(P,C)=178.8$ Hz], 70.40 [$^2J(P,C)=5.6$ Hz], 24.23 [$^3J(P,C)=3.9$ Hz], 24.01 [$^3J(P,C)=4.6$ Hz], 14.52 [$^2J(P,C)=9.0$ Hz]; ^{31}P NMR (202 MHz, $CDCl_3$): $\delta=20.33$; HR-MS (ESI): $m/z=305.1282$, calcd. for $C_{15}H_{23}O_3P$: 305.1277 [M+Na]$^+$ ($\Delta=1.6$ ppm); elemental analysis calcd. (%) for $C_{15}H_{23}O_3P$: C 63.82, H 8.21, P 10.97; found: C 63.52; H 8.16; P 10.94.

Diphenyl [(*E*)-1-methyl-2-phenylvinyl]phosphonate (3bb): Yellow oil; yield: 175 mg (50%). ^{1}H NMR (500.1 MHz,



$CDCl_3$, 25 °C, TMS): $\delta = 7.67$ [d, $^3J(P,H)_{cis} = 26.5$ Hz, 1H], 7.41–7.35 (m, 4H), 7.35–7.28 (m, 5H), 7.28–7.21 (m, 4H), 7.18–7.10 (m, 2H), 2.25 [d, $^3J(P,H) = 16.4$ Hz, 3H]; ^{13}C NMR (150.9 MHz, $CDCl_3$): $\delta = 150.60$ [$^2J(P,C) = 7.6$ Hz], 145.54 [$^2J(P,C) = 12.5$ Hz], 135.27 [$^3J(P,C) = 25.4$ Hz], 129.81, 129.64, 128.92, 128.56, 125.11, 124.7 [$^1J(P,C) = 181.1$ Hz], 120.58 [$^3J(P,C) = 4.5$ Hz], 14.60 [$^2J(P,C) = 9.0$ Hz]; ^{31}P NMR (202 MHz, $CDCl_3$): $\delta = 15.96$; HR-MS (ESI): $m/z = 351.1144$, calcd. for $C_{21}H_{19}O_3P$: 351.1145 $[M+H]^+$ ($\Delta = 0.3$ ppm); elemental analysis calcd. (%) for $C_{21}H_{19}O_3P$: C 71.99, H 5.47, P 8.84; found: C 71.69; H 5.37; P 8.70.

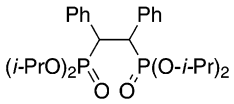
Didodecyl [(*E*)-1-methyl-2-phenylvinyl]phosphonate (3bc): Yellow oil; yield: 358 mg (67%). ^1H NMR



(500.1 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.46$ [d, $^3J(P,H)_{cis} = 24.8$ Hz, 1H], 7.41–7.35 (m, 4H), 7.35–7.26 (m, 1H), 4.15–3.90 (m, 4H), 2.06 [d, $^3J(P,H) = 15.3$ Hz, 3H], 1.77–1.61 (m, 4H), 1.48–1.14 (m, 36H), 0.95–0.83 (m, 6H); ^{13}C NMR (150.9 MHz, $CDCl_3$): $\delta = 142.68$ [$^2J(P,C) = 11.6$ Hz], 135.82 [$^3J(P,C) = 23.8$ Hz], 129.55, 128.47, 128.42, 126.05 [$^1J(P,C) = 178.5$ Hz], 65.95 [$^2J(P,C) = 5.7$ Hz], 32.03, 30.65, 30.61, 29.76, 29.74, 29.69, 29.66, 29.46, 29.30, 25.72, 22.80, 14.44 [$^2J(P,C) = 9.0$ Hz], 14.21; ^{31}P NMR (202 MHz, $CDCl_3$): $\delta = 22.67$; HR-MS (ESI): $m/z = 557.4087$, calcd. for $C_{33}H_{59}O_3P$: 557.4094 $[M+Na]^+$ ($\Delta = 1.3$ ppm); elemental analysis calcd. (%) for $C_{33}H_{59}O_3P$: C 74.11, H 11.12, P 5.79; found: C 74.03; H 11.02; P 5.69.

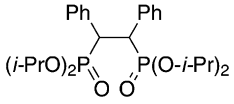
The compounds **3aa**, **3fa**, **3ab**, **3ac** were identified by comparison with the published spectral data.[15f]

***rac*-Tetraisopropyl (1,2-diphenylethane-1,2-diyl)bis(phosphonate) (*rac*-4aa):** Yellow oil; yield: 179 mg (35%).



^1H NMR (500.1 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.25$–7.07 (m, 10H), 4.83–4.66 (m, 2H), 4.41–4.25 (m, 2H), 3.89 [d, $^2J(P,H) = 9.5$ Hz, 2H], 1.43–1.26 (m, 12H), 1.16 [d, $J(H,H) = 6.2$ Hz, 6H], 0.71 [d, $J(H,H) = 6.2$ Hz, 6H]; ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 132.94$, 132.54, 127.37, 127.29, 71.72, 70.38, 45.71, 45.45, 44.89, 44.33, 44.07, 24.41, 24.15, 22.99; ^{31}P NMR (202 MHz, $CDCl_3$): $\delta = 25.68$; HR-MS (ESI): $m/z = 511.2366$, calcd. for $C_{26}H_{40}O_6P_2$: 511.2373 $[M+H]^+$ ($\Delta = 1.4$ ppm); elemental analysis calcd. (%) for $C_{26}H_{40}O_6P_2$: C 61.17, H 7.90, P 12.13; found: C 60.79; H 8.02, P 12.32.

***meso*-Tetraisopropyl (1,2-diphenylethane-1,2-diyl)bis(phosphonate) (*meso*-4aa):** White crystals; yield: 92 mg (18%). ^1H NMR (500.1 MHz, $CDCl_3$, 25 °C, TMS): $\delta =$



7.65–7.50 (m, 4H), 7.38–7.21 (m, 6H), 4.17–4.07 (m, 2H), 4.04–3.94 (m, 2H), 3.83 [dd, $^3J(P,H) = 3.0$ Hz, $^2J(P,H) = 7.7$ Hz, 2H], 1.06 [d, $J(H,H) = 6.1$ Hz, 6H], 0.99 [d, $J(H,H) = 6.1$ Hz, 6H], 0.63 [d, $J(H,H) = 6.1$ Hz, 6H], 0.43 [d, $J(H,H) = 6.1$ Hz, 6H]; ^{13}C NMR (125 MHz, $CDCl_3$): $\delta =$ 135.97, 131.03, 128.18, 127.39, 72.06, 69.41, 49.06, 48.70, 48.15, 47.59, 47.23, 24.65, 23.77, 23.32, 22.44; ^{31}P NMR (202 MHz, $CDCl_3$): $\delta = 25.23$; HR-MS (ESI): $m/z = 511.2379$, calcd. for $C_{26}H_{40}O_6P_2$: 511.2373 $[M+H]^+$ ($\Delta = 1.2$ ppm); elemental analysis calcd. (%) for $C_{26}H_{40}O_6P_2$: C 61.17, H 7.90, P 12.13; found: C 61.00; H 8.13; P 12.07. The determined molecular structure of *meso*-**4aa** is presented in Figure 2.

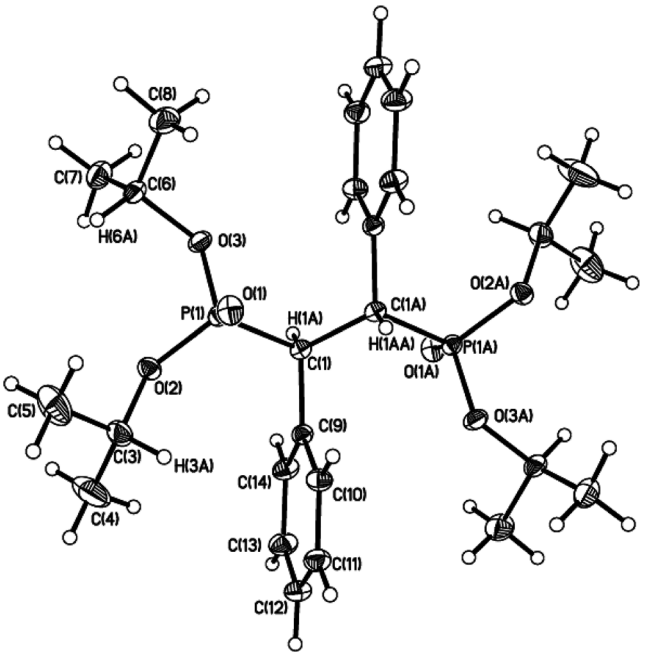
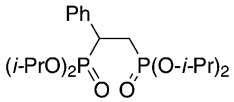


Figure 2. The molecular structure of *meso*-**4aa** determined by X-ray analysis.

CCDC 975404 contains the supplementary crystallographic data for *meso*-**4aa**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

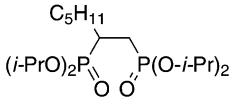
Tetraisopropyl (1-phenylethane-1,2-diyl)bis(phosphonate) (4ca): Yellow oil; yield: 163 mg (75%). ^1H NMR



(500.1 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.41$–7.34 (m, 2H), 7.31–7.19 (m, 3H), 4.72–4.60 (m, 1H), 4.56–4.46 (m, 1H), 4.46–4.29 (m, 2H), 3.44–3.29 (m, 1H), 2.51–2.32 (m, 2H), 1.32–1.27 (m, 6H), 1.21 [d, $J(H,H) = 6.1$ Hz, 3H], 1.18 [d, $J(H,H) = 6.1$ Hz, 3H], 1.13 [d, $J(H,H) = 6.1$ Hz, 3H], 1.05 [d, $J(H,H) = 6.1$ Hz, 3H], 0.98 [d, $J(H,H) = 6.1$ Hz, 3H], 0.83 [d, $J(H,H) = 6.1$ Hz, 3H]; ^{13}C NMR (125 MHz, $CDCl_3$): $\delta =$ 135.44, 129.82 [$^3J(P,C) = 5.7$ Hz], 128.12, 127.22, 71.61

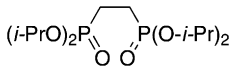
[^2J(P,C) = 6.0 Hz], 70.48 [^2J(P,C) = 6.4 Hz], 70.21 [^2J(P,C) = 5.6 Hz], 70.08 [^2J(P,C) = 5.6 Hz], 39.84 [^1J(P,C) = 134.7 Hz], 28.04 [^1J(P,C) = 140.0 Hz], 24.22, 23.91, 23.83, 23.56, 23.03; ^{31}P NMR (202 MHz, $CDCl_3$): δ = 27.20 [d, ^3J(P,P) = 82.5 Hz], 26.35 [d, ^3J(P,P) = 82.5 Hz]; HR-MS (ESI): m/z = 435.2063, calcd. for $C_{20}H_{36}O_6P_2$: 435.2060 $[M+H]^+$ (Δ = 0.7 ppm); elemental analysis calcd. (%) for $C_{20}H_{36}O_6P_2$: C 55.29, H 8.35, P 14.26; found: C 55.24; H 8.20; P 14.11.

Tetraisopropyl heptane-1,2-diylbis(phosphonate) (4da): Yellow oil; yield: 150 mg (70%). ^{1}H NMR (500.1 MHz,



$CDCl_3$, 25 °C, TMS): δ = 4.75–4.62 (m, 4H), 2.22–1.87 (m, 3H), 1.82–1.55 (m, 4H), 1.55–1.45 (m, 1H), 1.45–1.33 (m, 1H), 1.33–1.06 (m, 26H), 0.92–0.71 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 70.22 [^2J(P,C) = 8.2 Hz], 32.07, 32.05 [^1J(P,C) = 141.5 Hz], 28.94, 26.96, 26.38 [^1J(P,C) = 140.3 Hz], 24.08, 22.49, 14.06; ^{31}P NMR (202 MHz, $CDCl_3$): δ = 31.18 [d, ^3J(P,P) = 78.3 Hz], 28.92 [d, ^3J(P,P) = 78.3 Hz]; HR-MS (ESI): m/z = 429.2524, calcd. for $C_{19}H_{42}O_6P_2$: 429.2529 $[M+H]^+$ (Δ = 1.2 ppm).

Tetraisopropyl ethane-1,2-diylbis(phosphonate) (4ea): Yellow oil; yield: 116 mg (65%). ^{1}H NMR (500.1 MHz,



$CDCl_3$, 25 °C, TMS): δ = 4.76–4.62 (m, 4H), 1.95–1.88 (m, 4H), 1.32 [d, J(H,H) = 6.2 Hz, 24H]; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 70.49, 24.06, 21.51, 21.17, 20.62, 20.06, 19.72; ^{31}P NMR (202 MHz, $CDCl_3$): δ = 28.55; HR-MS (ESI): m/z = 381.1557, calcd. for $C_{14}H_{32}O_6P_2$: 381.1566 $[M+Na]^+$ (Δ = 2.4 ppm); elemental analysis calcd. (%) for $C_{14}H_{32}O_6P_2$: C 46.92, H 9.00, P 17.29; found: C 46.64; H 9.15; P 17.13.

Acknowledgements

Department of Structural Studies of Zelinsky Institute of Organic Chemistry, RAS and Alexey Kashin are acknowledged for recording SEM images. This research was supported by Russian Foundation for Basic Research (grants 12-03-31518 and 13-03-01210).

References

[1] a) G. W. Rabe, H. Komber, L. Häussler, K. Kreger, G. Lattermann, *Macromolecules* **2010**, *43*, 1178–1181; b) S. Salzinger, U. B. Seemann, A. Plikhta, B. Rieger, *Macromolecules* **2011**, *44*, 5920–5927; c) N. Zhang, S. Salzinger, B. Rieger, *Macromolecules* **2012**, *45*, 9751–9758.

[2] a) M. Banks, J. R. Ebdon, M. Johnson, *Polymer* **1994**, *35*, 3470–3473; b) D. Price, K. Pyrah, T. R. Hull, G. J. Milnes, J. R. Ebdon, B. J. Hunt, P. Joseph, *Polym. Degrad. Stab.* **2002**, *77*, 227–233; c) S.-Y. Lu, I. Hamerton, *Prog. Polym. Sci.* **2002**, *27*, 1661–1712.

[3] a) T. Minami, J. Motoyoshiya, *Synthesis* **1992**, 333–349; b) V. M. Dembitsky, A. A. A. A. Quntar, A. Haj-Yehia, M. Srebnik, *Mini Rev. Org. Chem.* **2005**, *2*, 91–109; c) R. A. Stockland Jr, R. I. Taylor, L. E. Thompson, P. B. Patel, *Org. Lett.* **2005**, *7*, 851–853.

[4] a) J. P. Krise, V. J. Stella, *Adv. Drug Delivery Rev.* **1996**, *19*, 287–310; b) E. De Clercq, A. Holý, *Nat. Rev. Drug Discovery* **2005**, *4*, 928–940; c) J. T. Whitteck, W. Ni, B. M. Griffin, A. C. Eliot, P. M. Thomas, N. L. Kelleher, W. W. Metcalf, W. A. van der Donk, *Angew. Chem.* **2007**, *119*, 9247–9250; *Angew. Chem. Int. Ed.* **2007**, *46*, 9089–9092; d) E. De Clercq, *Biochem. Pharmacol.* **2011**, *82*, 99–109.

[5] a) N. S. Goulioukina, T. M. Dolgina, I. P. Beletskaya, J.-Ch. Henry, D. Lavergne, V. Ratovelomanana-Vidal, J.-P. Genêt, *Tetrahedron: Asymmetry* **2001**, *12*, 319–327; b) N. S. Gulyukina, T. M. Dolgina, G. N. Bondarenko, I. P. Beletskaya, N. A. Bondarenko, J.-C. Henry, D. Lavergne, V. Ratovelomanana-Vidal, J.-P. Genêt, *Russ. J. Org. Chem.* **2002**, *38*, 573–587; c) N. S. Goulioukina, T. M. Dolgina, G. N. Bondarenko, I. P. Beletskaya, M. M. Ilyin, V. A. Davankov, A. Pfaltz, *Tetrahedron: Asymmetry* **2003**, *14*, 1397–1401; d) P. Cheruku, A. Paptchikhine, T. L. Church, P. G. Andersson, *J. Am. Chem. Soc.* **2009**, *131*, 8285–8289.

[6] a) V. Ojea, S. Conde, M. Ruiz, M. C. Fernández, J. M. Quintela, *Tetrahedron Lett.* **1997**, *38*, 4311–4314; b) M. Ruiz, M. C. Fernández, A. Diáz, J. M. Quintela, V. Ojea, *J. Org. Chem.* **2003**, *68*, 7634–7645.

[7] a) C. Thomsen, *Gen. Pharmacol.* **1997**, *29*, 151–158; b) D. D. Schoepp, D. E. Jane, J. A. Monn, *Neuropharmacology* **1999**, *38*, 1431–1476; c) S. Lopez, N. Turle-Lorenzo, F. Acher, E. De Leonibus, A. Mele, M. Amalric, *J. Neurosci.* **2007**, *27*, 6701–6711; d) A. C. Vernon, V. Zbarsky, K. P. Datla, D. T. Dexter, M. J. Croucher, *J. Pharmacol. Exp. Ther.* **2007**, *320*, 397–409.

[8] a) H. Fleisch, *Endocr. Rev.* **1998**, *19*, 80–100; b) R. G. G. Russell, *Ann. N. Y. Acad. Sci.* **2006**, *1068*, 367–401; c) R. G. G. Russell, N. B. Watts, F. H. Ebetino, M. J. Rogers, *Osteoporosis Int.* **2008**, *19*, 733–759; d) M. T. Drake, B. L. Clarke, S. Khosla, *Mayo Clin. Proc.* **2008**, *83*, 1032–1045.

[9] a) E. T. K. Haupt, J. Kopf, J. Petrova, V. Arabadzhiev, S. Momchilova, *Heteroat. Chem.* **2006**, *17*, 36–46; b) J. R. Dilworth, S. J. Parrott, *Chem. Soc. Rev.* **1998**, *27*, 43–55; c) J. S. Preston, A. C. du Preez, *Solvent Extr. Ion Exch.* **1998**, *16*, 687–706; d) N. Margiotta, R. Ostuni, D. Teoli, M. Morpurgo, N. Realdon, B. Palazzo, G. Natile, *Dalton Trans.* **2007**, 3131–3139.

[10] R. G. G. Russell, M. J. Rogers, J. C. Frith, S. P. Luckman, F. P. Coxon, H. L. Benford, P. I. Croucher, C. Shipman, H. A. Fleisch, *J. Bone Miner. Res.* **1999**, *14*, 53–65, and references cited therein.

[11] a) D. Bosbach, P. V. Coveney, J. L. W. Griffin, A. Putnis, P. Risthaus, S. Stackhouse, A. Whiting, *J. Chem. Soc. Perkin Trans. 2* **2002**, 1238–1245; b) K. D. Demadis, in: *Progress in Solid State Chemistry Research*, (Ed.: R. W. Buckley), Nova Science Publishers, Inc., New York, **2007**, pp 109–172.

[12] a) C. Hogue, *Chem. Eng. News* **2012**, *90 (44)*, 34–37; b) C. Hogue, *Chem. Eng. News* **2012**, *90 (32)*, 30–31; c) C. Hogue, *Chem. Eng. News* **2013**, *91 (14)*, 6.
[13] a) I. P. Beletskaya, M. A. Kazankova, *Russ. J. Org. Chem.* **2002**, *38*, 1391–1430; b) M. Tanaka, *Top. Curr. Chem.* **2004**, *232*, 25–54; c) F. Alonso, I. P. Beletskaya, M. Yus, *Chem. Rev.* **2004**, *104*, 3079–3160; d) I. P. Beletskaya, M. M. Kabachnik, *Mendeleev Commun.* **2008**, *18*, 113–120; e) L. Coudray, J.-L. Montchamp, *Eur. J. Org. Chem.* **2008**, 3601–3613; f) D. S. Glueck, *Top. Organomet. Chem.* **2010**, *31*, 65–100; g) Q. Xu, L.-B. Han, *J. Organomet. Chem.* **2011**, *696*, 130–140; h) I. P. Beletskaya, V. P. Ananikov, L. L. Khemchyan, in: *Phosphorus compounds: advanced tools in catalysis and material sciences*, Vol. 37, (Eds.: M. Peruzzini, L. Gonsalvi), Springer, London, **2011**, pp 213–264; i) M. Tanaka, *Top. Organomet. Chem.* **2013**, *43*, 167–202.
[14] Selected examples of Pd-catalyzed hydrophosphorylation of alkynes: a) L.-B. Han, M. Tanaka, *J. Am. Chem. Soc.* **1996**, *118*, 1571–1572; b) N. S. Gulykina, T. M. Dolgina, G. N. Bondarenko, I. P. Beletskaya, *Russ. J. Org. Chem.* **2003**, *39*, 797–807; c) N. Dobashi, K. Fuse, T. Hoshino, J. Kanada, T. Kashiwabara, C. Kobata, S. K. Nune, M. Tanaka, *Tetrahedron Lett.* **2007**, *48*, 4669–4673; d) V. P. Ananikov, L. L. Khemchyan, I. P. Beletskaya, *Synlett* **2009**, 2375–2381; e) T. Mizuta, C. Miyaji, T. Katayama, J.-I. Ushio, K. Kubo, K. Miyoshi, *Organometallics* **2009**, *28*, 539–546; f) Q. Xu, R. Shen, Y. Ono, R. Nagahata, S. Shimada, M. Goto, L.-B. Han, *Chem. Commun.* **2011**, *47*, 2333–2335; g) V. P. Ananikov, J. V. Ivanova, L. L. Khemchyan, I. P. Beletskaya, *Eur. J. Org. Chem.* **2012**, 3830–3840.
[15] Selected examples of Rh-catalyzed hydrophosphorylation of alkynes: a) Ch.-Q. Zhao, L.-B. Han, M. Goto, M. Tanaka, *Angew. Chem.* **2001**, *113*, 1983–1986; *Angew. Chem. Int. Ed.* **2001**, *40*, 1929–1932; b) J. F. Reichwein, M. C. Patel, B. L. Pagenkopf, *Org. Lett.* **2001**, *3*, 4303–4306; selected examples of Ni-catalyzed hydrophosphorylation of alkynes: c) L.-B. Han, C. Zhang, H. Yazawa, S. Shimada, *J. Am. Chem. Soc.* **2004**, *126*, 5080–5081; d) L.-B. Han, Y. Ono, H. Yazawa, *Org. Lett.* **2005**, *7*, 2909–2911; e) V. P. Ananikov, L. L. Khemchyan, I. P. Beletskaya, *Russ. J. Org. Chem.* **2010**, *46*, 1269–1276; f) V. P. Ananikov, L. L. Khemchyan, I. P. Beletskaya, Z. A. Starikova, *Adv. Synth. Catal.* **2010**, *352*, 2979–2992; g) A. Fadel, F. Legrand, G. Evano, N. Rabasso, *Adv. Synth. Catal.* **2011**, *353*, 263–267.
[16] A. Allen Jr, D. R. Manke, W. Lin, *Tetrahedron Lett.* **2000**, *41*, 151–154.
[17] For the dehydrogenative double phosphorylation see: L.-B. Han, Y. Ono, S. Shimada, *J. Am. Chem. Soc.* **2008**, *130*, 2752–2753.
[18] a) K. Moedritzer, R. R. Irani, *J. Inorg. Nucl. Chem.* **1961**, *22*, 297–304; b) M. Murray, K. M. Higgins, G. Hägele, A. Gaedcke, J. Mikroyannidis, *Phosphorus Sulfur Silicon Relat. Elem.* **1990**, *48*, 117–130; c) H. Beckmann, G. Grossmann, G. Ohms, *Magn. Reson. Chem.* **1992**, *30*, 860–864.
[19] a) K. Fischer, K. Jonas, P. Misbach, R. Stabba, G. Wilke, *Angew. Chem.* **1973**, *85*, 1001–1012; *Angew. Chem. Int. Ed. Engl.* **1973**, *12*, 943–953; b) Y. Sato, M. Takimoto, M. Mori, *J. Am. Chem. Soc.* **2000**, *122*, 1624–1634.
[20] See the Supporting Information for additional details.
[21] A. Kraszewski, J. Stawinski, *Pure Appl. Chem.* **2007**, *79*, 2217–2227.
[22] Note that alkyne **1a**, being able to donate electron density to the metal due to presence of triple bond, can stabilize the active Ni species as well. See Section 2.1. of the Supporting Information.
[23] a) V. P. Ananikov, I. P. Beletskaya, *Chem. Asian J.* **2011**, *6*, 1423–1430; b) V. P. Ananikov, A. V. Makarov, I. P. Beletskaya, *Chem. Eur. J.* **2011**, *17*, 12623–12630.
[24] a) P. W. Jolly, G. Wilke, *The Organic Chemistry of Nickel,* Academic Press, New York, **1974**; b) T. Masuda, F. Sanda, M. Shiotsuki, *Polymerization of Acetylenes*, in: *Comprehensive Organometallic Chemistry III*, Vol. 11, (Eds.: D. M. P. Mingos, R. H. Crabtree), Elsevier, Oxford, **2007**, pp 557–593.
[25] A. S. Kashin, V. P. Ananikov, *Russ. Chem. Bull. Int. Ed.* **2011**, *60*, 2602–2607.
[26] D. S. Pedersen, C. Rosenbohm, *Synthesis* **2001**, 2431–2434.

