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An efficient and recyclable silica-supported carbene–Cu(II) catalyst for the oxidative coupling reaction of terminal alkynes with *H*-phosphonates under base-free reaction conditions

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The oxidative coupling reactions of terminal alkynes with *H*-phosphonates were explored using SiO_2–NHC–Cu(II) (5.0 mol%) as catalyst at room temperature under base-free reaction conditions. The reactions of a variety of terminal alkynes with *H*-phosphonates generated the corresponding alkynylphosphonate products in good to excellent yields. In addition, SiO_2–NHC–Cu(II) could be recovered and recycled for six consecutive trials without significant loss of its reactivity. Copyright © 2011 John Wiley & Sons, Ltd.

Supporting information may be found in the online version of this article.

Keywords: NHC–Cu(II); terminal alkynes; *H*-phosphonates; recyclibility; silica-supported catalyst

Introduction

Alkynylphosphonates, as important topical phosphorus element scaffolds for the construction of structurally sophisticated phosphorus compounds, are broadly found in bioactive natural products and therapeutic molecules.[1] Therefore, considerable effort has been made to develop efficient strategies for preparing them. In general, reaction of $(RO)_2P(O)Cl$ with Li or Mg acetylene is one of the most common and efficient methods for the synthesis of alkynylphosphonates, but it suffers from the use of hazardous chemicals and lack of functionality tolerance.[2] Recently, Zhao *et al*. described a practical copper-catalyzed aerobic oxidative coupling of terminal alkynes with *H*-phosphonates to generate the corresponding alkynylphosphonate products.[3] The reaction represents a novel and efficient strategy for the synthesis of alkynylphosphonates using transition metal-catalyzed oxidative C–P cross-coupling. Although the reaction materials, terminal alkynes and *H*-phosphonates are commercially available, base is still necessary. To eliminate the base used in the reaction, the search for an efficient and practical catalytic system remains a challenge.

Transition metal complexes of *N*-heterocyclic carbenes (NHCs) have attracted great interest because the strongly σ-donating NHCs offer a good opportunity to tune the reactivity and selectivity of transition metal catalysts.[4] Their ability to strongly coordinate to the metal center allows for the formation of stable metal species facilitating catalyst design efforts.

Since the first stable *N*-heterocyclic carbene (NHC) isolated by Arduengo *et al*. in 1991, NHCs have emerged as a class of ligands in metal-mediated reactions due to their strong σ-donor properties compared with phosphine ligands, thereby enhancing the stability of NHC complexes toward heat and moisture.[5] A large number of NHC complexes of precious metals have been prepared and characterized. Their catalytic applications in various organic transformations, including C–C bond and C–N bond formations,[6,7] olefin metathesis,[8] oligomerization and polymerization of alkenes,[9] have been studied widely. The most successful application at present appears to be the use of palladium complexes of NHC as ligands in C–C and C–heteroatom cross-coupling reactions. In contrast, although the first NHC–Cu(I) complex was reported in 1993 by Arduengo *et al*.,[10] the chemistry of NHC–Cu(I) and NHC–Cu(II) complexes has been relatively less studied compared with other coinage metals and NHC. The investigation and application of NHC–Cu(II) complexes remain relatively rare. The first NHC–Cu(II) complex, which was presumably formed through addition of free NHC to a Cu(II) source in the catalyzed conjugate addition of $ZnEt_2$ to enones, was reported by Fraser and Woodward.[11] Yun reported the NHC–Cu(II) complex, $(IPr)Cu(II)(OAc)_2$ (IPr = 1,3-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene) as an efficient pre-catalyst for the 1,2- and 1,4-reduction of carbonyl compounds under hydrosilylation reaction conditions.[12]

N-Heterocyclic carbenes (NHCs) have proven to be excellent supporting ligands in transition metal-mediated reactions.[13] For the reaction of Cu-catalyzed oxidative coupling of terminal alkynes with *H*-phosphonates, Cu species have been proposed to be responsible for the formation of a copper acetylide intermediate, which is then reacted with *H*-phosphonates to give the oxidative coupling

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product based on previous studies.[3] We envisioned NHC−Cu(I) and NHC−Cu(II) complexes working as efficient and convenient pre-catalysts for the oxidative cross-coupling of terminal alkynes with *H*-phosphonates. Indeed, copper-catalyzed oxidative coupling reactions of terminal alkynes with various substrates, such as polyfluoroarenes, amides, ureas, *N*-alkyl-arylsulfonamides, heterocycles and aldehyde–amine, have been documented in the literature.[14]

Although homogeneous catalysts have many advantages, they are difficult to recover and reuse. Furthermore, residual catalyst metal along with the products could induce serious problems in the synthesis of bioactive and functional substrates. It could not be used in large-scale synthesis, particularly on environmental and economic concerns. However, immobilization of transition metal complexes onto solid supports is one way to make such catalysis practical. The use of silica substrates for catalysis has attracted a surge of interest due to their superior mechanical and thermal stability, excellent recyclability and convenient separation.[15]

In previous work, we found that polystyrene or SiO_2-supported–NHC complexes are highly effective for cyclo-addition and coupling reactions.[16] Herein, we wish to report an efficient C−P bond oxidative cross-coupling reaction of terminal alkynes with *H*-phosphonates catalyzed by a reusable silica immobilized NHC−Cu (II) catalyst. It is noteworthy that SiO_2−NHC−Cu(II) catalyst could catalyze aerobic oxidative C−P cross-coupling reaction of terminal alkynes with *H*-phosphonates in the absence of any base. In addition, SiO_2−NHC−Cu(II) catalyst could be reused at least six times without significant loss of its catalytic activity (Scheme 1).

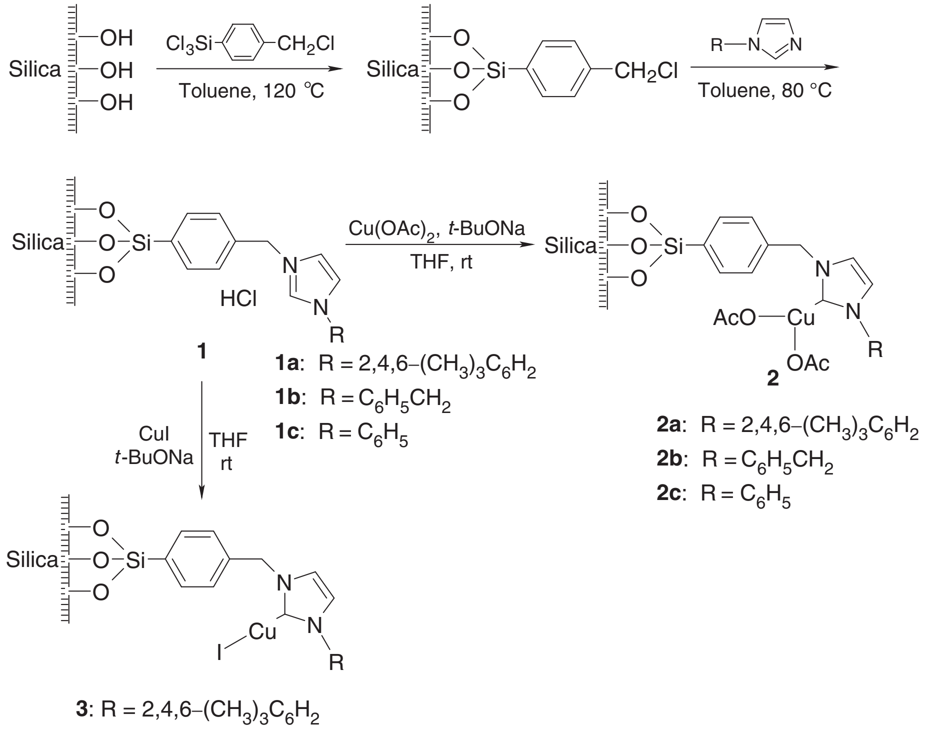
Experimental

Materials and Methods

All ^1H and ^{13}C NMR studies were performed in $CDCl_3$ and recorded on a Bruker Avance NMR 400 spectrometer. ^1H NMR spectra were collected at 400 MHz using a 6000 Hz spectral width, a relaxation delay of 3.5 s, a pulse width of 38°, 30 k data points, and residual $CDCl_3$ (7.26 ppm) as an internal reference. ^{13}C NMR spectra were collected at 100 MHz using a 25 000 Hz spectra width, a relaxation delay of 1.5 s, 75 k data points, a pulse width of 40°, and residual $CDCl_3$ (77.00 ppm) as the internal reference. The C, H, and N analyses were performed with a Vario El III Elementar. The Cu content was determined by an atomic absorption spectroscopy analysis (Z-5000, Hitachi). Products were purified by flash column chromatography on 200–400 mesh silica gel, SiO_2. The chemicals were purchased from commercial suppliers (Aldrich, USA and Shanghai Chemical Company, China) and were used without purification prior to use. All the reactions were carried out under an air atmosphere, and commercially obtained materials were used without further purification. The benzyl chloride functionalized silica, silica-supported ionic liquid **1a**, **1b**, and **1c** were prepared according to the literature.[14a] The loading of the silica-supported ionic liquid **1a**, **1b**, and **1c** were quantified by CHN microanalysis based on the N content and found to be 1.10 mmol g^{-1}, 0.81 mmol g^{-1}, and 0.87 mmol g^{-1} respectively.

Preparation of SiO_2−NHC−Cu(II) Catalyst 2a

In an oven-dried Schlenk flask, freshly prepared silica-supported ionic liquid **1a** (1.0 g), *t*-BuONa (0.096 g, 1.0 mmol), $Cu(OAc)_2$ (0.181 g, 1.0 mmol) and toluene (5.0 ml) were added. The resulting suspension was stirred at room temperature for 12 h. Then the solution was filtered, and the solid was washed with toluene (3.0 ml), methanol (3.0 ml), acetone (3.0 ml), and dried under vacuum at 60 °C for 12 h. SiO_2−NHC−Cu(II) catalyst **2a** was obtained as a green powder (1.09 g). The copper content of **2a** was found to be 1.00 mmol g^{-1} based on atomic absorption spectroscopy (AAS) analysis. IR (KBr): 3451, 3110, 2963, 2913, 1603, 1540, 1480, 1378, 1226, 1097, 1043, 930, 852, 750 cm^{-1}.



Scheme 1. Preparation of SiO_2−NHC−Cu(II) and SiO_2−NHC−Cu(I) catalysts

Preparation of SiO_2–NHC–Cu(II) Catalyst 2b

The synthesis of **2b** was similar to that of **2a**, except that silica-supported ionic liquid **1b** (1.0 g) was used instead of **1a**. SiO_2–NHC–Cu(II) catalyst **2b** was obtained as a green powder (1.05 g). The copper content of **2b** was found to be 0.78 mmol g^{-1} based on AAS analysis. IR (KBr): 3301, 3150, 3066, 2965, 2872, 2826, 2748, 1717, 1595, 1537, 1443, 1336, 1261, 1200, 1108, 1058, 942, 809, 764 cm^{-1}.

Preparation of SiO_2–NHC–Cu(II) Catalyst 2c

The synthesis of **2c** was similar to that of **2a**, except that silica-supported ionic liquid **1c** (1.0 g) was used instead of **1a**. SiO_2–NHC–Cu(II) catalyst **2c** was obtained as a green powder (1.07 g). The copper content of **2c** was found to be 0.83 mmol g^{-1} based on atomic absorption spectroscopy AAS analysis. IR (KBr): 3447, 3149, 3074, 2965, 2871, 1596, 1547, 1488, 1448, 1228, 1201, 853, 756, 720 cm^{-1}.

Preparation of SiO_2–NHC–Cu(I) catalyst 3

The synthesis of **3** was similar to that of **2a**, except that CuI (0.190 g, 1.0 mmol) was used instead of $Cu(OAc)_2$ (0.181 g, 1.0 mmol). SiO_2–NHC–Cu(I) catalyst **3** was obtained as a gray powder (1.14 g). The copper content of **3** was found to be 0.87 mmol g^{-1} based on AAS. IR (KBr): 3474, 2963, 2916, 1536, 1462, 1398, 1336, 1110, 1069, 947, 808, 757 cm^{-1}.

General Procedure for the Reaction of Terminal Alkynes with *H*-Phosphonates

An oven-dried round-bottomed flask was charged with SiO_2–NHC–Cu(II) catalyst **2a** (50 mg, 0.05 mmol), terminal alkyne (1.0 mmol), *H*-phosphonate (1.2 mmol) and dimethyl sulfoxide (DMSO) (2.0 ml). The mixture was stirred at room temperature for 24 h under air. The progress of the reaction was monitored by thin-layer chromatography. On completion of the reaction, the mixture was filtered, and the solution was concentrated under reduced pressure and purified by column chromatography on silica gel (hexane:EtOAc = 3:1) to afford the pure alkynylphosphonate.

Diethyl[(phenyl)ethynyl]phosphonate (**6a**),[3] diethyl[(4-methylphenyl)ethynyl]phosphonate (**6b**),[17] diethyl[(4-methoxylphenyl) ethynyl]phosphonate (**6 d**),[17] diethyl[(4-fluorophenyl)ethynyl] phosphonate (**6e**),[18] [diethyl(4-chlorophenyl)ethynyl]phosphonate (**6f**),[19] diethyl[(3-aminophenyl)ethynyl]phosphonate (**6 h**),[17] diethyl[(4-phenylphenyl)ethynyl]phosphonate (**6j**),[18] diethyl (3-pyridinylethynyl)phosphonate (**6 k**),[20] di(isopropyl)[(phenyl)ethynyl]phosphonate (**6 l**),[3] diethyl-1-heptynylphosphonate (**6 m**),[21] diethyl-1-hexynylphosphonate (**6n**),[17] diethyl-3-(benzyloxy)-1-propynylphosphonate (**6o**),[22] and diethyl(ethoxycarbonyl) phosphonate (**6p**),[23] have been characterized by comparing their ^1H and ^{13}C spectral data (see Supporting Information) with those reported in the literature.

Diethyl[(4-*tert*-butylphenyl)ethynyl]phosphonate (**6c**): yellow oil. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.52$–7.50 (m, 2H, Ar–H), 7.40 (d, $J = 8.8$ Hz, 2H, Ar–H), 4.27–4.19 (m, 4H, $-CH_2CH_3$), 1.41 (t, $J = 6.8$ Hz, 6H, $-CH_2CH_3$), 1.32 (s, 9H, ^{t}Bu–Ar). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 154.3$, 132.4 (d, $J_{C-P} = 2.5$ Hz), 125.5, 116.3 (d, $J_{C-P} = 5.6$ Hz), 99.5 (d, $J_{C-P} = 53.0$ Hz), 77.6 (d, $J_{C-P} = 298.8$ Hz), 63.1 (d, $J_{C-P} = 5.5$ Hz), 35.0, 30.9 (d, $J_{C-P} = 6.7$ Hz), 16.0 (d, $J_{C-P} = 7.0$ Hz). Elemental analysis: calc. for $C_{16}H_{23}PO_3$ C, 65.29; H, 7.88; found C, 65.05; H, 8.19. HRMS (ESI): calc. for $C_{16}H_{23}PO_3$ $[M]^+$ 294.1384; found 294.1382.

[Diethyl(4-bromphenyl)ethynyl]phosphonate (**6 g**): yellow oil. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.52$ (d, $J = 8.4$ Hz, 2H, Ar–H), 7.42 (d, $J = 8.4$ Hz, 2H, Ar–H), 4.25–4.21 (m, 4H, $-CH_2CH_3$), 1.42 (t, $J = 7.2$ Hz, 6H, $-CH_2CH_3$). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 133.9$ (d, $J_{C-P} = 2.5$ Hz), 131.9, 125.5, 118.4 (d, $J_{C-P} = 5.6$ Hz), 97.7 (d, $J_{C-P} = 52.7$ Hz), 79.6 (d, $J_{C-P} = 297.5$ Hz), 63.3 (d, $J_{C-P} = 5.5$ Hz), 16.0 (d, $J_{C-P} = 7.0$ Hz). Elemental analysis: calc. for $C_{12}H_{14}BrPO_3$ C, 45.45; H, 4.45; found C, 45.15; H, 4.68. HRMS (ESI): calc. for $C_{12}H_{14}BrPO_3$ $[M]^+$ 315.9867; found 315.9868.

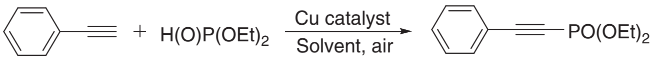
[Diethyl(2-bromophenyl)ethynyl]phosphonate (**6i**): yellow oil. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.64$–7.58 (m, 2H, Ar–H), 7.34–7.30 (m, 2H, Ar–H), 4.31–4.23 (m, 4H, $-CH_2CH_3$), 1.42 (t, $J = 6.8$ Hz, 6H, $-CH_2CH_3$). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 134.5$ (d, $J_{C=P} = 2.5$ Hz), 132.7, 131.7, 127.2, 126.1 (d, $J_{C-P} = 2.8$ Hz), 122.2, 97.9 (d, $J_{C-P} = 52.6$ Hz), 63.5 (d, $J_{C-P} = 5.6$ Hz), 16.1 (d, $J_{C-P} = 7.1$ Hz). Elemental analysis: calc. for $C_{12}H_{14}BrPO_3$ C, 45.45; H, 4.45; found C, 45.28; H, 4.72. HRMS (ESI): calc. for $C_{12}H_{14}BrPO_3$ $[M]^+$ 315.9867; found 315.9862.

Results and Discussion

In our initial screening experiments, the oxidative C–P cross-coupling reaction of terminal alkyne with *H*-phosphonate was catalyzed by SiO_2–NHC–Cu(II) (**2a**) (Table 1, entry 1). The reaction of phenylacetylene with diethyl hydrogen phosphate (model reaction) was carried out in the presence of 5.0 mol% **2a** at room temperature for 24 h. The formation of diethyl phenylethynylphosphonate was confirmed by ^1H and ^{13}C NMR spectroscopic analysis of the obtained product. To our surprise, the model reaction was completed in the presence of SiO_2–NHC–Cu(II) complex, **2a** as catalyst without base, and the isolated yield of the product was observed to be 90% (with 3.21 of standard deviation) (Table 1, entry 1). In a similar manner, SiO_2–NHC–Cu(I) **3** was also found to be effective for the reaction, and a comparable product yield to that of SiO_2–NHC–Cu(II) **2b**, and **2c** was obtained, inferior to that of SiO_2–NHC–Cu(II) **2a** as catalyst (Table 1, entries 2–4). The influence of the substituted group of NHC in SiO_2–NHC–Cu(II) complexes on their catalytic activity for the model reaction was found to be 2,4,6-$(CH_3)_3C_6H_2$ (**2a**) > $C_6H_5CH_2$ (**2b**) > C_6H_5 (**2c**) (Table 1, entries 1–3). It is obvious that the catalytic activity of SiO_2–NHC–Cu(II) complexes decreases for the oxidative-coupling reaction along with the steric hindrance of substituted group decreases. From Table 1, it is evident that **2a** is the best catalyst for this coupling reaction.

The effect of copper salt on the model reaction in the absence of *N*-heterocyclic carbene (NHC) was also investigated. When the model reaction was catalyzed by $Cu(OAc)_2$ without ligand and base, 55% yield (with 2.43 of standard deviation) of the desired oxidative-coupling product was isolated (Table 1, entry 5). However, additional K_2CO_3 as base did not improve the yield of desired product, but decreased the yield of the product (Table 1, entry 6). When CuI was used as catalyst in the model reaction, 81% (with 1.97 of standard deviation) and 80% (with 2.58 of standard deviation) yields of the coupling products were isolated in the presence of K_2CO_3 and Et_3N as bases in the reaction, respectively, similar to the results reported in the literature[3] (Table 1, entries 8 and 9). Unfortunately, only trace amounts of desired product were detected when the reaction was carried out in the presence of CuI as catalyst without base (Table 1, entry 7).

Table 1. Effect of catalyst and solvent on the oxidative C—P cross-coupling of terminal alkyne with *H*-phosphonate[a]



Entry	Catalyst	Solvent	Yield[b] (%)/SD
1	**2a**	DMSO	90/3.21
2	**2b**	DMSO	69/2.65
3	**2c**	DMSO	61/4.17
4	**2d**	DMSO	65/1.78
5	$Cu(OAc)_2$	DMSO	55/2.43
6	$Cu(OAc)_2$	DMSO	29[c]/3.01
7	CuI	DMSO	Trace
8	CuI	DMSO	81[c]/1.97
9	CuI	DMSO	80[d]/2.58
10	$(IPr)Cu(OAc)_2$[e]	DMSO	91/2.96
11	$(IPr)Cu(OAc)_2$[e]	DMSO	89[c]/3.01
12	(IPr)CuI[e]	DMSO	83/2.54
13	(IPr)CuI[e]	DMSO	80[c]/2.17
14	**2a**	DMF	0
15	**2a**	THF	0
16	**2a**	Toluene	0
17	**2a**	Methanol	0

[a] Reaction conditions: Cu catalyst (containing Cu 0.05 mmol), phenylacetylene (1.0 mmol), diethyl hydrogen phosphate (1.2 mmol) was carried out in solvent (2.0 ml) at room temperature for 24 h under air.

[b] Isolated yield and standard deviation (SD) obtained from three times.

[c] In the presence of K_2CO_3 as base.

[d] In the presence of Et_3N as base.

[e] IPr = 1,3-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene).

Furthermore, the oxidative C—P cross-coupling reactions of terminal alkyne with *H*-phosphonate catalyzed by the NHC—Cu(I)/(II) complexes under homogeneous conditions were also investigated. It was found that the coupling reaction could be finished under homogeneous conditions in the present or absence of base, which gives the desired product in good yield (Table 1, entries 10–13). Finally, SiO_2—NHC—Cu(II) **2a** was selected as catalyst for the following reaction without additional base considering the highly efficient and recyclable catalyst used, and environment friendliness.

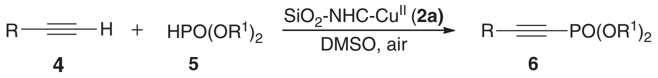
The effects of solvents on the model reaction were also examined in the presence of SiO_2—NHC—Cu(II) **2a** as catalyst. The use of DMSO as solvent gave the best results among the solvents including DMF, THF, toluene, and methanol. It is important to note that no desired cross-coupling product was isolated when the reaction was carried out in DMF, THF, toluene, or methanol (Table 1, entries 14–17). A similar solvent effect was also observed in the literature.[3,24] With respect to the effective catalyst loading, 5.0 mol% SiO_2—NHC—Cu(II) **2a** was found to be optimal. When less than 5.0 mol% of SiO_2—NHC—Cu(II) **2a** was used, the reaction did not go to completion. However, no significant improvements were observed with more 5.0 mol% SiO_2—NHC—Cu(II) **2a** used in the reaction.

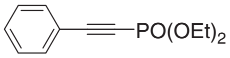
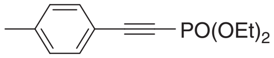
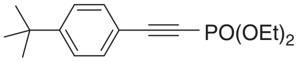
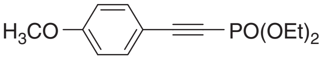
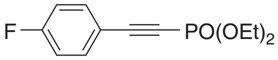
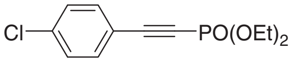
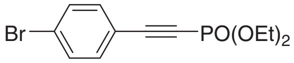
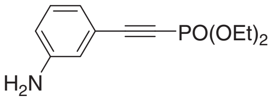
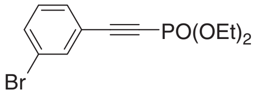
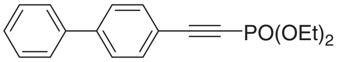
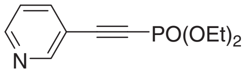
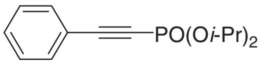
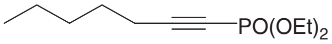
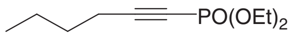
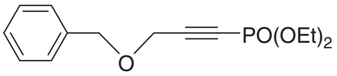
Under the optimized reaction conditions, the oxidative C=P cross-coupling reaction of substituted phenylacetylenes with *H*-phosphonates compounds was then investigated using **2a** as the catalyst. The results are summarized in Table 2. Various substituted phenylacetylene derivatives bearing either electron-donating or electron-withdrawing functional groups, such as Cl, Br, CH_3, OCH_3, C_6H_5, *tert*-C_4H_9 and NH_2, on the phenyl rings could be reacted with diethyl hydrogen phosphate smoothly to generate the corresponding functionalized alkynylphosphonates in good yields (Table 2, entries 1–10). It is worth noting that the oxidative cross-coupling of terminal alkynes with *H*-phosphonate is relatively insensitive to the electronic characteristics of a substituent as well as its location in the aromatic terminal alkyne, and led to good yields.[3]

Most important, we also find that aliphatic alkynes, such as 1-hexyne and 1-heptyne, will also undergo oxidative carbon–phosphorus bond cross-coupling smoothly with excellent yields. It is superior to terminal aromatic alkynes used as substrates (Table 2, entries 13 and 14 vs. entries 1–10). Fortunately, ethyl propiolate and 3-(benzyloxy)-1-propyne also gave high yields of oxidative-coupling products with diethyl hydrogen phosphate (Table 2, entries 15 and 16). The scope of this reaction was extended to heteroaryl alkynes, such as 3-ethynylpyridine, with good results also obtained (Table 2, entry 11). Besides diethyl hydrogen phosphate, the *H*-phosphonate diisopropyl hydrogen phosphate was also used as reaction partner with phenylacetylene, and the result indicated that 91% yield of the corresponding di(isopropyl)-phenylethynylphosphonate **6 l** was isolated under the present reaction conditions (Table 2, entry 12).

The recyclability and reusability of SiO_2—NHC—Cu(II) catalyst **2a** was also investigated. After the reaction, the catalyst **2a** was separated by simple filtration and washed. After drying, it could be reused directly without further purification. The recovered catalyst was used in the next run and almost consistent activity was observed for six consecutive cycles (Table 3). Meanwhile, copper leaching in SiO_2—NHC—Cu(II) catalyst **2a** was determined. AAS analysis of the clear filtrates obtained by filtration after the reaction indicated that Cu content was <0.3 ppm.

Table 2. SiO_2–NHC–Cu(II)-catalyzed oxidative coupling of terminal alkynes with *H*-phosphonates[a]



Entry	Product	Yield[b] (%)/SD
1	 **6a**	90/3.21
2	 **6b**	73/1.56
3	 **6c**	82/2.63
4	 **6d**	78/4.21
5	 **6e**	68/4.31
6	 **6f**	70/4.13
7	 **6g**	76/3.25
8	 **6h**	80/3.86
9	 **6i**	75/2.75
10	 **6j**	81/1.19
11	 **6k**	77/3.47
12	 **6l**	91/1.26
13	 **6m**	96[c]/2.57
14	 **6n**	95[c]/2.76
15	 **6o**	95[c]/3.58
16	$C_2H_5O_2C$—≡—$PO(OEt)_2$ **6p**	87/2.27

[a] Reaction conditions: SiO_2–NHC–Cu(II) **2a** (50 mg, containing Cu 0.05 mmol, 5 mol%), terminal alkyne (1.0 mmol), and *H*-phosphonate (1.2 mmol) was carried out in DMSO (2.0 ml) at room temperature for 24 h under air.

[b] Isolated yield and standard deviation (SD) obtained from three times.

[c] Reaction for 12 h.

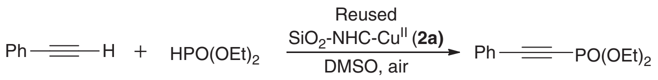
Conclusions

The efficient and recyclable silica-supported carbene–Cu(II) complex SiO_2–NHC–Cu(II) **2a** as catalyst for aerobic oxidative coupling of terminal alkynes with *H*-phosphonates in the absence of any base at room temperature has been developed. The reactions of a variety of terminal alkynes with *H*-phosphonates generated the corresponding alkynylphosphonate products in good to excellent yields. In addition, SiO_2–NHC–Cu(II) **2a** could be recycled by filtration and reused six times without apparent loss of catalytic activity. Thus this method constitutes an economical and environmentally benign process for the synthesis of alkynylphosphonate compounds.

SUPPORTING INFORMATION

Supporting information may be found in the online version of this article.

Table 3. Successive trials using recoverable SiO_2–NHC–Cu(II) catalyst[a]



Trial	Yield[b](%)/SD	Trial	Yield[b] (%)/SD
1	90/2.37	4	87/2.42
2	89/2.69	5	85/3.47
3	88/2.54	6	83/3.97

[a] Reaction conditions: SiO_2–NHC–Cu(II) **2a** (50 mg, containing Cu 0.05 mmol), phenylacetylene (1.0 mmol), and diethyl hydrogen phosphate (1.2 mmol) was carried out in DMSO (2.0 ml) at room temperature for 24 h under air.

[b] Isolated yield and standard deviation (SD) obtained from three times.

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