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Triaryl phosphine-functionalized *N*-heterocyclic carbene ligands for Heck reaction

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Abstract—A new type of triaryl phosphine-functionalized imidazolium salts **6** were prepared. Their palladium complexes, generated in situ, were successfully applied in the palladium-catalyzed Heck reaction. Using 1 mol% of Pd(dba)$_2$ and 1 mol% **6c** in the presence of 2 equiv of K_2CO_3 in DMAc has proven to be highly efficient for the coupling of a wide array of aryl bromides and iodides with acrylates in excellent yield. The coupling of 4-bromotoluene with various styrene derivatives catalyzed by Pd/**6c** complex also gave good results.

1. Introduction

Heck reaction has received intensive studies over the past several decades.[1] Especially the palladium-catalyzed arylation and vinylation have proven to be one of the most powerful means for the formation of carbon–carbon bond in organic synthesis.[2] Usually, Heck reaction is carried out in the presence of phosphine ligands, which stabilize the active palladium intermediates[3] and assist the initial oxidative-addition of C–X bonds.[4] Excellent results have been reported for the palladium-catalyzed Heck reactions when sterically bulky monophosphines,[5] diphosphines,[6] cyclometalated phosphines[7] or phosphites are used as ligands.[8] However, the phosphine ligands and the phosphine–palladium complexes are liable to air and moisture at elevated temperature, placing significant limits on their synthetic application. Therefore, in view of practical use, the development of more reactive and stable ligands is of importance for the palladium-catalyzed Heck reaction.

Recently, nucleophilic N-heterocyclic carbenes (NHC's),[9] with a stronger σ-donor electronic property than bulky tertiary phosphines,[10] have emerged as a new family of ligands. In contrast to metal complexes of phosphines, the metal–NHC complexes appeared to be extraordinarily stable toward heat, air and moisture due to their high dissociation energies of the metal–carbon bond.[11] This superiority of NHC's made them a potential type of ligands for Heck reaction. Since Herrmann[12] reported the first application of palladium–NHC complex in Heck reaction in 1995, various palladium complexes with monodente carbenes, chelating dicarbenes or tridentate pincer bis-carbenes, and even donor-functionalized NHC's have been synthesized and used as catalysts for the Heck reaction.[13] Most of the donor-functionalized NHC ligands had a N-donor, such as pyridine, imine or oxazoline as pendant groups. However, little attention has been paid to the synthesis of phosphine-functionalized NHC ligands,[14] though the theoretical calculation suggested that the chelating phosphine–carbene Pd complex might be a suitable catalyst for the Heck reaction.[15] So far as we know, there was one successful application of phosphine–NHC ligand in Heck reaction, which was reported by Nolan and co-workers.[14c] Herein, we describe the synthesis of a new type of phosphine-functionalized NHC ligands with stable triaryl phosphines as pendant functional groups and their application in palladium-catalyzed Heck reaction. The results revealed that the palladium-NHC species generated in situ from phosphine-functionalized imidazolium salts and Pd(dba)$_2$ in the presence of K_2CO_3 were highly effective for the coupling of a wide range of bromides and iodides with acrylates and the coupling of aryl bromides with styrene derivatives.

2. Result and discussion

2.1. Synthesis of phosphine-functionalized imidazolium salts

Initially, we attempted to synthesize triaryl phosphine-functionalized imidazolium salts **6** via the direct reduction

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Keywords: Carbenes; Heck reaction; Palladium; Phosphine-functionalized.

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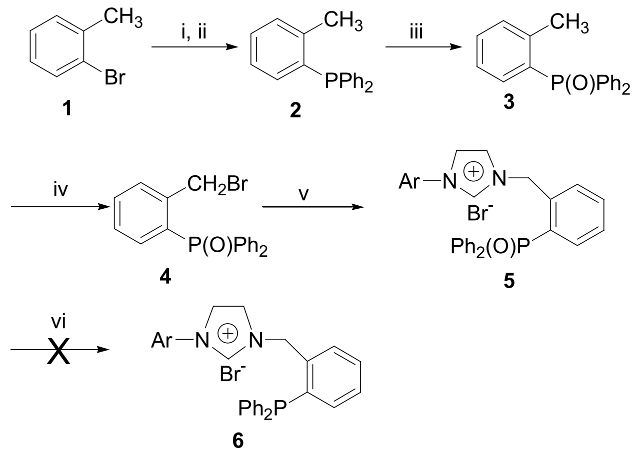
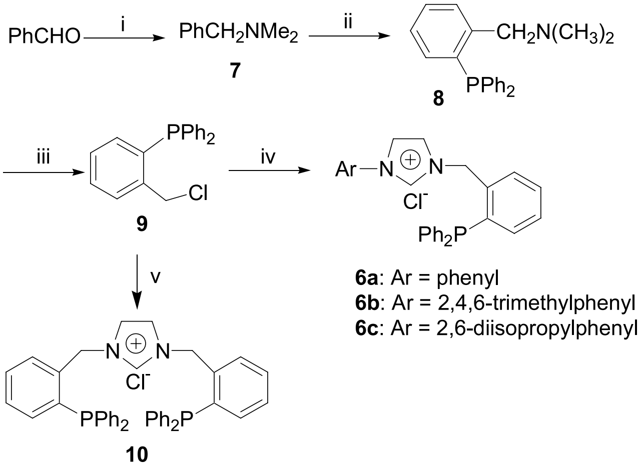


Scheme 1. Reagents and conditions: (i) Mg, THF, reflux; (ii) PPh_2Cl, −78 °C to room temperature; (iii) H_2O_2, CH_2Cl_2, room temperature; (iv) NBS, AIBN, CCl_4, reflux; (v) 1-arylimidazole, EtOH (abs), reflux; (vi) Cl_3SiH, EtOH, toluene, 120 °C.

of the phosphinoxide **5**[14d] (Scheme 1). Diphenyl-*o*-tolylphosphane (**2**), prepared from coupling of Ph_2PC1 with Grinard reagent of 2-bromotoluene, was treated with H_2O_2 to form the corresponding phosphinoxide **3** in excellent yield (97% for three steps). Bromination of compound **3** with NBS in the presence of AIBN provided *o*-(diphenylphosphinyl)-benzyl bromide (**4**) in 65% yield. Then, alkylation of 1-arylimidazole with bromide **4** gave imidazolium salts **5** in 70% yield. However, the direct reduction of compound **5** with Cl_3SiH was unsuccessful. Use of other reducing reagents, such as methyldichlorosilane, also gave disappointing results. It was very likely that the bulky steric effect around the phosphorus atom in compound **5** hindered its interaction with the reducing reagent.

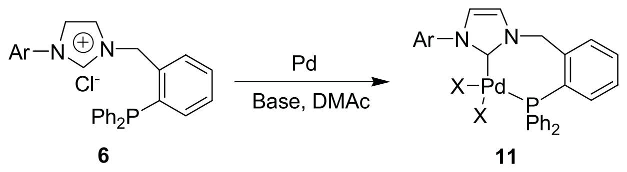
Another synthetic route was then designed to make phosphine-functionalized imidazolium salts **6**, which started from benzaldehyde (Scheme 2). The benzaldehyde was condensed with dimethylamine, followed by the reduction with $NaBH_4$ to give benzyldimethylamine (**7**). Compound **7** was *ortho*-metallated by *n*-BuLi and reacted with Ph_2PC1 to afford 2-(diphenylphosphino)benzyldimethylamine (**8**). In the presence of ethyl chloroformate, **8** was converted to the key intermediate *o*-(diphenylphosphino)benzyl chloride (**9**) at refluxing condition. The yield was 42% for the three steps. Subsequently, alkylation of 1-arylimidazole with compound **9** in refluxing ethanol gave triaryl phosphine-functionalized imidazolium salts **6** in the yields of 46–63%. By using K_2CO_3 as the base, tridentate imidazolium salt **10** was obtained from 1*H*-imidazole and the compound **9** in 32% yield.



Scheme 2. Reagents and conditions: (i) (a) Me_2NH_2Cl, Ti(O*i*-Pr)$_4$, NEt_3, EtOH (abs), room temperature; (b) $NaBH_4$, room temperature; (ii) (a) *n*-BuLi, Et_2O, room temperature; (b) Ph_2PCl, Et_2O, −78 °C to room temperature; (iii) $ClCO_2Et$, benzene, reflux; (iv) 1-arylimidazole, EtOH (abs), reflux; (v) 1*H*-imidazole, K_2CO_3, EtOH (abs), reflux.

2.2. Heck reaction

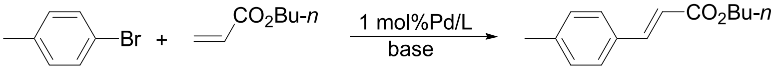
2.2.1. Arylation of acrylates. Having prepared the new phosphine-functionalized imidazolium salts **6** and **10**, we firstly tested the catalytic activity of the palladium complexes **11**[16] (Scheme 3) for the Heck reaction of *p*-tolyl bromide with *n*-butyl acrylate (Scheme 3). Preliminary experiment in DMAc in the presence of Cs_2CO_3 as the base at 120 °C showed that the catalyst **11a** generated in situ was efficient to yield coupling product (Table 1, entry 1). Controlled experiment indicated that the coupling reaction did not take place in the absence of imidazolium salt **6a**. A systematic investigation on the substituent effect in the imidazolium salts **6** indicated that the introduction of alkyl groups to the *N*-phenyl ring of NHC ligands notably increased the reaction rate and the yield of product, and imidazolium salt **6c** was found to be the most reactive one (entries 2 and 3). But the tridentate phosphine-functionalized imidazolium salt **10** showed a poor reactivity in this reaction (entry 4). As a comparison, the phosphinoxide **5b** was also tested for the reaction and poorer catalytic activity (24 h, 67% yield) was observed, indicating that the pendant phosphine group in ligands **6** is necessary for having a high reactivity.



Scheme 3.

Various palladium compounds, such as $Pd(dba)_2$, $Pd(OAc)_2$, $[Pd[(\eta\text{-}C_3H_5)Cl]]_2$ and $Pd_2(dba)_3\cdot CHCl_3$, were compared as catalyst precursors under the same reaction conditions (1 mol% [Pd], 1 mol% **6c**, 1 equiv *p*-tolyl bromide, 1.5 equiv *n*-butyl acrylate, 2.0 equiv Cs_2CO_3 and DMAc as solvent at 120 °C) (Table 1). The results showed that $Pd(dba)_2$ was the choice of catalyst precursor, which gave 100% conversion in the shortest reaction time (entry 3). The ratio of imidazolium salt **6c** to palladium precursor was also studied. The ratio of 1:1 was found to be optimal. When the ratio of **6c**/Pd changed from 1:1 to 2: 1, the coupling product was obtained in only 29% yield (entry 8). Further increasing the ratio to 3:1 or 4:1 led a very slow reaction (entries 9 and 10). These results suggested that NHC ligand **6c** coordinated to palladium with two coordinating atoms to form a chelating complex. When the ratio of **6c**/Pd exceeded 2:1, two bidentate P–C ligands occupied all of the four

Table 1. Heck reaction of 4-bromotoluene and *n*-butyl acrylate under various conditions[a]



Entry	Pd	Ligand	L/Pd	Base	Solvent	Time (h)	Conv. (%)[b]	Yield (%)[c]
1	$Pd(dba)_2$	**6a**	1	Cs_2CO_3	DMAc	18	91	62
2	$Pd(dba)_2$	**6b**	1	Cs_2CO_3	DMAc	14	99	82
3	$Pd(dba)_2$	**6c**	1	Cs_2CO_3	DMAc	12	100	85
4	$Pd(dba)_2$	**10**	1	Cs_2CO_3	DMAc	24	22	ND[d]
5	$Pd(OAc)_2$	**6c**	1	Cs_2CO_3	DMAc	24	54	28
6	$[Pd[(\eta\text{-}C_3H_5)Cl]]_2$	**6c**	1	Cs_2CO_3	DMAc	24	88	41
7	$Pd_2(dba)_3\cdot CHCl_3$	**6c**	1	Cs_2CO_3	DMAc	18	98	57
8	$Pd(dba)_2$	**6c**	2	Cs_2CO_3	DMAc	12	100	29
9	$Pd(dba)_2$	**6c**	3	Cs_2CO_3	DMAc	24	18	ND
10	$Pd(dba)_2$	**6c**	4	Cs_2CO_3	DMAc	24	5	ND
11	$Pd(dba)_2$	**6c**	1	NEt_3	DMAc	24	11	ND
12	$Pd(dba)_2$	**6c**	1	KOAc	DMAc	24	45	39
13	$Pd(dba)_2$	**6c**	1	K_3PO_4	DMAc	24	98	65
14	$Pd(dba)_2$	**6c**	1	KOH	DMAc	24	7	ND
15	$Pd(dba)_2$	**6c**	1	KF	DMAc	24	14	ND
16	$Pd(dba)_2$	**6c**	1	Na_2CO_3	DMAc	24	65	54
17	$Pd(dba)_2$	**6c**	1	K_2CO_3	DMAc	12	93	93
18[e]	$Pd(dba)_2$	**6c**	1	K_2CO_3	DMAc	11	99	99
19	$Pd(dba)_2$	**6c**	1	K_2CO_3	DMF	12	83	75
20	$Pd(dba)_2$	**6c**	1	K_2CO_3	DMSO	12	74	50
21	$Pd(dba)_2$	**6c**	1	K_2CO_3	Dioxane	24	56	39

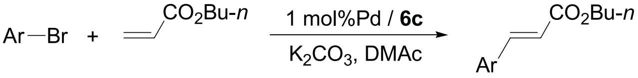
[a] Reaction conditions: 1 mol% [Pd], 1 mol% **6c**, 1 equiv *p*-tolyl bromide, 1.5 equiv *n*-butyl acrylate, 2.0 equiv base at 0.5 M at 120 °C.
[b] Determined by GC.
[c] Isolated yield.
[d] Not determined.
[e] At 140 °C.

coordination sites of palladium, hindering the oxidative addition of *p*-tolyl bromide to palladium, and consequently resulted in a slow or even no reaction. The base was found to significantly influence both the reaction rate and the yield of product. The highest yield was achieved by using K_2CO_3 (entry 17). Other inorganic bases, such as KOH, KF, KOAc, Na_2CO_3 and K_3PO_4, and organic base NEt_3 gave the coupling product in low yields (entries 11–16). The reaction was also solvent dependent when using K_2CO_3 as the base. DMAc was found to be the choice of solvent. Increasing the temperature from 120 to 140 °C accelerated the reaction rate and the yield of product (entry 18).

At the optimal reaction conditions, a wide array of aryl bromides bearing electron-donating or electron-withdrawing groups can react with *n*-butyl acrylate providing coupling products in excellent yields. As can be seen in the Table 2, most of the aryl bromides with electron-withdrawing substituents, such as CF_3, CN or NO_2, reacted completely at 120 °C in less than 6 h. While for the aryl bromides with electron-donating substituents, complete conversions were achieved only at 140 °C. These results showed that the electron-deficient bromides were beneficial to the reaction. The steric effect of substrates was also obvious. For the sterically congested substrates, such as 1-bromo-3,5-di-*tert*-butylbenzene (entry 6) and 1-bromo-3,5-di-*tert*-butyl-4-methoxybenzene (entry 9), longer reaction time were required. 1-Bromo-2-methyl naphthalene, another sterically congested bromide, could also couple with *n*-butyl acrylate using our catalyst system in high yield (entry 10). These results showed that the carbene ligands generated in situ from phosphine-functionalized imidazolium salt **6** have an activity, which is superior or comparable to the sterically demanding *ortho*-substituted arylphosphines, $P(o\text{-tol})_3$[17] and the monodentate carbenes IMes.[18] It was noteworthy that in the coupling reaction of aryl bromides bearing another halide group, such as F or Cl, the mono-coupling products were formed predominantly. The bis-coupling products were isolated in just 3 and 7% yields in the reaction of *ortho*- and *para*-chlorophenyl bromides (entries 17 and 19). However, the reaction of dibromides, with excess *n*-butyl acrylate, produced di-coupling products in quantitative yields (entries 20 and 21). Bromides bearing carbonyl groups can couple with *n*-butyl acrylate leaving carbonyl group unchanged (entries 22 and 23). The aryl iodides had higher reactivities than bromides in the coupling reaction with *n*-butyl acrylate. The reactions were complete in 2 h at 120 °C and the yields were excellent (entries 24, 25 and 26). Double arylation products could be obtained in high yields when excess iodides were used (entries 27–29). However the reaction of aryl chlorides, such as 1-chloro-4-nitrobenzene and 2-chlorobenzaldehyde, with *n*-butyl acrylate provided very little amount of desired coupling products using Pd/**6c** system at the same conditions. Besides *n*-butyl acrylate, methyl acrylate and ethyl acrylate can also efficiently react with *p*-tolyl bromide providing the corresponding coupling products in 86 and 99% yields, respectively.

2.2.2. Arylation of styrenes. Using the same reaction conditions, we further studied the Heck reaction of 4-bromotoluene with styrene using in situ generated palladium complexes of phosphine-functionalized NHC ligands. The results are summarized in Table 3. Arylation

Table 2. Heck reaction of aryl bromides and iodides with *n*-butyl acrylate under optimal reaction conditions[a]



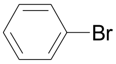
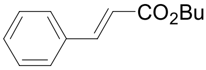
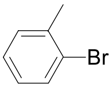
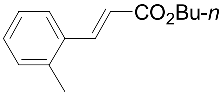
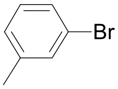
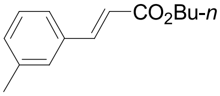
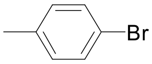
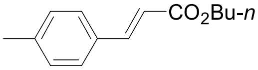
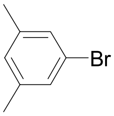
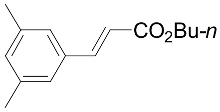
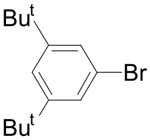
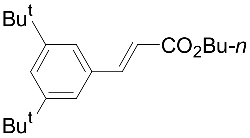
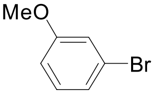
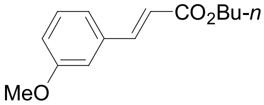
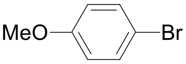
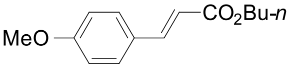
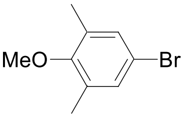
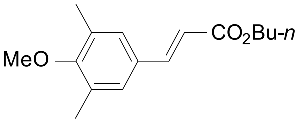
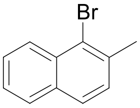
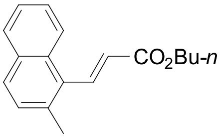
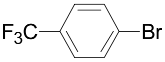
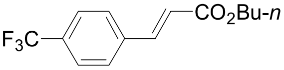
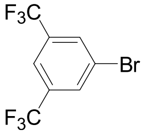
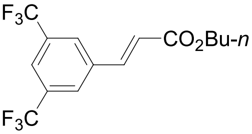
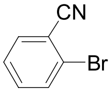
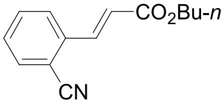
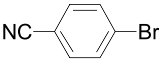
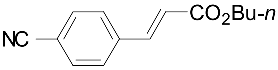
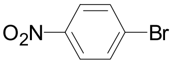
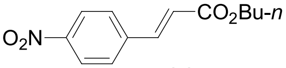
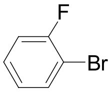
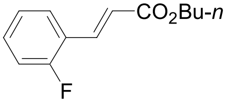
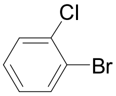
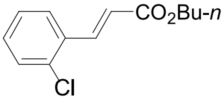
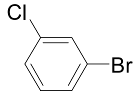
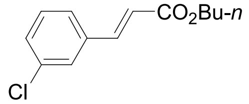
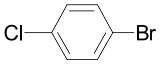
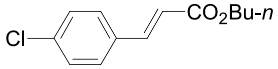
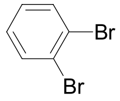
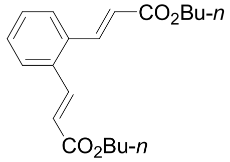
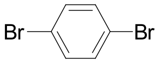
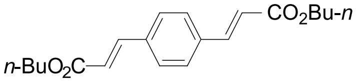
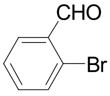
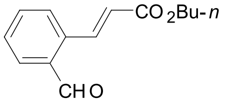
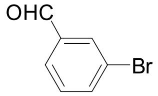
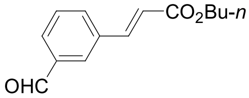
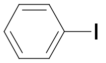
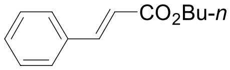
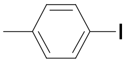
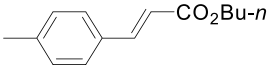
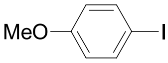
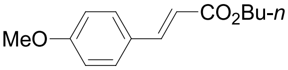
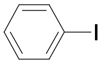
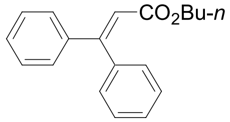
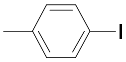
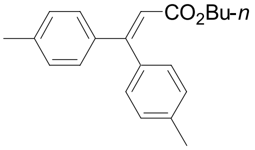
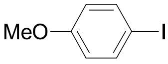
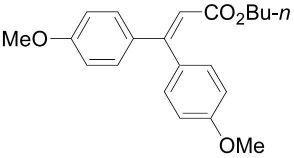
Entry	Aryl halide	Temperature (°C)	Time (h)	Conv. (%)[b]	Product	Yield (%)[c]	Ref.
1		140	11	99		99	19
2		140	12	100		98	17
3		140	12	100		98	20
4		140	11	99		99	18
5		140	12	100		98	18
6		140	24	100		100	21
7		140	12	100		100	18
8		140	12	100		96	18
9		140	24	100		94	22
10		140	24	100		100	23
11		120	6	100		99	24
12		120	6	100		96	25
13		120	10	97		89	23
14		120	5	100		93	18
15		120	6	100		85	25
16		120	6	97		92	25
17		120	10	96		87[d]	26

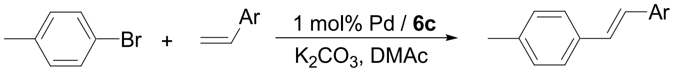
Table 2 (*continued*)

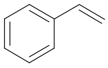
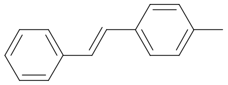
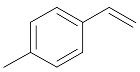
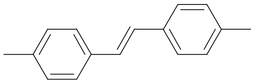
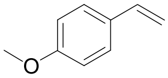
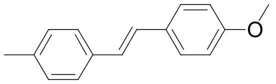
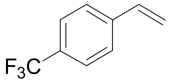
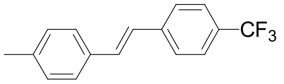
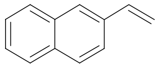
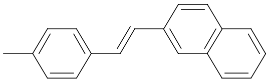
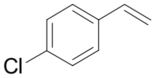
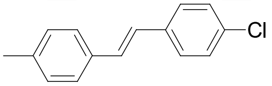
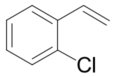
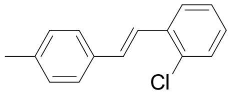
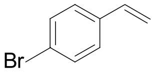
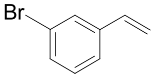
Entry	Aryl halide	Temperature (°C)	Time (h)	Conv. (%)[b]	Product	Yield (%)[c]	Ref.
18		120	5	100		100	27
19		120	5	100		93[e]	13a
20[f]		120	16	99		99	28
21[f]		120	12	100		99	28
22		120	12	100		83	23
23		120	5	100		93	29
24		120	2	100		97	19
25		120	2	100		92	18
26		120	2	100		93	18
27[g]		140	60	100		93	30
28[g]		140	140	100		99	30
29[g]		140	45	100		100	30

[a] Performed with 1.5 equiv acrylate, L/Pd = 1, 2.0 equiv base; 0.5 M.
[b] Determined by GC.
[c] Isolated yield.
[d] 3% Di-coupled product was obtained.
[e] 7% Di-coupled product was obtained.
[f] 4.0 equiv acrylate, 5.0 equiv base.
[g] 4.0 equiv halide, 5.0 equiv base.

of styrene with 4-bromotoluene at 140 °C gave 100% conversion and offered 96% yield of the coupling product (entry 1). A variety of styrene derivatives with electron-donating or electron-withdrawing groups on the phenyl ring were tested, and 100% conversions with good to excellent yields were obtained within 12 h. This revealed that the Pd catalysts bearing a chelating phosphine-functionalized NHC ligand were comparably good as the Pd catalysts containing a monodentate NHC ligand and a triarylphosphine in the arylation reaction of styrenes.[31] 4-Chlorostyrene was an exception, however, which gave a lower yield of coupling product (74%, entry 6). In the reaction of bromo-substituted styrenes, such as 4-bromostyrene and 3-bromostyrene, no cross-coupling products were isolated. On the contrary, the self-coupling of bromostyrenes occurred to form polymer PPV.[32] The lower yield in the reaction of 4-chlorostyrene can be also ascribed to some extent to its polymerization as a precipitation of a yellow solid was observed at the end of the reaction.

Table 3. Heck reaction of 4-bromotoluene with styrene derivatives[a]



Entry	Olefin	Product	Yield (%)[b]	Ref.
1			96	33
2			96	34
3			93	35
4			91	36
5			91	37
6			74^{c}	38
7			99	39
9		Polymer	—	32
10		Polymer	—	32

[a] Performed with 1.5 equiv olefin, L/Pd = 1, 2.0 equiv base, 0.5 M, 140 °C, 12 h.

[b] Isolated yield.

[c] Polymer was observed.

3. Conclusion

In summary, we have developed a new type of efficient triaryl phoshphine-funtionalized NHC ligands for the palladium-catalyzed Heck reactions. These phosphine-functionalized imidazole carbene ligands were easily prepared. Their palladium complexes, generated in situ, were applicable to the coupling reaction of bromides and iodides with acrylates and the coupling reaction of styrene derivatives with 4-bromotoluene in high yields. In these Heck reactions, the bulky substituents on the *N*-phenyl ring of the phoshphine-functionalized NHC ligands were found to be beneficial to the high activity of the catalyst. This might suggest that the introduction of bulky groups to the *P*-phenyl rings of the phoshphine-funtionalized NHC ligands is also helpful to increase the activity of the Pd catalyst, which is in progress in our laboratory.

4. Experimental

4.1. General

All reactions and manipulations were performed in an argon-filled glovebox or using standard Schlenk techniques, unless otherwise indicated. The aryl halides and styrene derivatives were purchased from Aldrich Co. or Acros Co. and used as received, with the exception of 2-bromotoluene, 3-bromotoluene and 4-bromotoluene, which were distilled prior to use. $Pd(OAc)_2$ and $[Pd[(\eta\text{-}C_3H_5)Cl]]_2$ were purchased from Acros Co. $Pd(dba)_2$ and $Pd_2(dba)_3 \cdot CHCl_3$ were prepared according to the reported procedures.[40] Absolute EtOH was distilled from magnesium ethylate. 1,4-Dioxane was distilled from sodium benzophenone ketyl. Anhydrous DMSO, DMF, DMAc were freshly distilled from calcium hydride. K_3PO_4 was ground to a fine powder and dried in a vacuum oven prior to use. Cs_2CO_3, K_2CO_3, Na_2CO_3, KF, KOAc and KOH were used as received. NEt_3 was redistilled prior to use. ^1H, ^{13}C and ^{31}P NMR spectra were recorded in $CDCl_3$ on Varian Mercury Vx-300 spectrometers. HRMS were recorded on APEX II spectrometer. GC analyses were performed using a Hewlett Packard Model HP 6890 Series with HP-5 column.

4.1.1. Synthesis of 3-phenyl-1-(2-diphenylphosphinobenzyl)-3*H*-imidazol-1-ium chloride (6a). Under an atmosphere of argon, 8 mL abs. EtOH was added to a Schlenk tube charged with 1-phenylimidazole (288 mg, 2.0 mmol) and *o*-(diphenylphosphino)benzyl chloride (0.64 g, 2.05 mmol). The mixture was allowed to stir at 80 °C for 2 days. The ethanol was then removed under vacuum. The residue was purified by a flash chromatography

(CH_2Cl_2/MeOH) to give **6a** as a white solid (0.42 g, 46% yield). ^{1}H NMR δ 5.96 (s, 2H, CH_2), 6.90 (m, 1H, NCHCHN), 7.08–7.63 (m, 19H, Ar-H), 8.04 (m, 1H, NCHCHN), 11.12 (s, 1H, NCHN); ^{31}P NMR δ −16.58 (s); ^{13}C NMR δ 51.8, 52.1, 119.8, 121.9, 122.7, 122.8, 129.0, 129.1, 129.6, 130.3, 130.7, 130.8, 132.6, 132.7, 133.8, 134.1, 134.6, 134.7, 135.0, 135.1, 136.9, 137.0, 137.4, 137.8; HRMS for $C_{28}H_{24}N_2P^+$ $[M-Cl]^+$, calcd: 419.1672; found: 419.1672.

4.1.2. Synthesis of 3-mesityl-1-(2-diphenylphosphinobenzyl)-3*H*-imidazol-1-ium chloride (6b). The compound **6b** was prepared in 60% yield by the same procedure described for **6a** using 1-mesitylimidazole. ^{1}H NMR δ 2.02 (s, 6H, CH_3), 2.33 (s, 3H, CH_3), 6.20 (s, 2H, CH_2), 6.95 (s, 1H, Ar-H), 6.98 (s, 3H, Ar-H), 7.24–7.38 (m, 11H, Ar-H), 7.46 (m, 1H, NCHCHN), 7.59 (s, 1H, Ar-H), 8.11 (m, 1H, NCHCHN), 10.87 (s, 1H, NCHN); ^{31}P NMR δ −14.89 (s); ^{13}C NMR δ 17.8, 21.3, 51.1, 51.4, 122.6, 122.7, 129.1,129.2, 129.7, 130.0, 130.3, 131.0, 132.2, 132.3, 133.7, 133.9, 134.2, 134.5, 135.0, 135.1, 136.0, 136.5, 136.7, 136.9, 138.1, 138.5, 139.0, 141.4; HRMS for $C_{31}H_{30}N_2P^+$ $[M-Cl]^+$, calcd: 461.2141; found: 461.2143.

4.1.3. Synthesis of 3-(2,6-diisopropylphenyl)-1-(2-diphenylphosphinobenzyl)-3*H*-imidazol-1-ium chloride (6c). The compound **6c** was prepared in 63% yield by the same procedure described for **6a** using 1-(2,6-diisopropylphenyl)-imidazole. ^{1}H NMR δ 1.11 (d, $J=7.2$ Hz, 6H, CH_3), 1.23 (d, $J=7.2$ Hz, 6H, CH_3), 2.26 (m, 2H, CH), 6.26 (s, 2H, CH_2), 6.98 (m, 1H, NCHCHN), 7.00 (s, 1H, Ar-H), 7.24–7.55 (m, 15H, Ar-H), 7.75 (s, 1H, Ar-H), 8.14 (m, 1H, NCHCHN), 10.84 (s, 1H, NCHN); ^{31}P NMR δ −14.48 (s); ^{13}C NMR δ 24.4, 24.6, 28.7, 28.9, 51.1, 51.3, 122.7, 122.8, 123.6, 124.9, 129.2, 129.3, 129.7, 130.0, 130.5, 130.9, 132.1, 132.2, 133.9, 134.2, 135.0, 136.5, 136.7, 138.3, 138.6, 139.4, 145.6; HRMS for $C_{34}H_{36}N_2P^+$ $[M-Cl]^+$, calcd: 503.2610; found: 503.2609.

4.1.4. Synthesis of 1,3-bis(2-diphenylphosphinobenzyl)-imidazolidin-1-ium chloride (10). Under an atmosphere of argon, imidazole (0.20 g, 3.0 mmol), *o*-(diphenylphosphino)benzyl chloride (1.90 g 6.1 mmol) and K_2CO_3 (0.42 g 3.0 mmol) were mixed in 20 mL abs EtOH and refluxed for 2 days. The solvent was removed in vacuum, and the residue was extracted with CH_2Cl_2. After drying over $MgSO_4$, the solvent was removed under vacuum, and the residue was purified by a flash chromatography (CH_2Cl_2/MeOH) to give **10** as a white solid (0.62 g, 32% yield). ^{1}H NMR δ 5.58 (s, 4H, CH_2), 6.89 (s, 4H, Ar-H), 6.95–7.46 (m, 22H, Ar-H), 7.70 (s, 2H, Ar-H), 7.74 (m, 2H, NCHCHN), 10.39 (s, 1H, NCHN); ^{31}P NMR δ −15.49 (s); ^{13}C NMR δ 51.4, 51.7, 121.7, 121.8, 129.1, 129.2, 129.5, 129.7, 130.3, 130.7, 131.6, 131.7, 133.8, 134.1, 134.7, 134.8, 135.3, 136.8, 136.9, 137.0, 137.2, 137.6; HRMS for $C_{41}H_{35}N_2P_2^+$ $[M-Cl]^+$, calcd: 617.2270; found: 617.2265.

4.2. General procedure for the Heck reaction of aryl halides with olefins

Under an atmosphere of argon, 2.0 mL DMAc was injected to a Schlenk tube charged with $Pd(dba)_2$ (0.01 mmol), imidazolium salt (0.01 mmol), and K_2CO_3 (2.0 mmol). The mixture was stirred for 30 min at 25 °C and then added 1.0 mmol of aryl halide, 1.5 mmol of olefin successively. The Schlenk tube was placed in a 120 °C or 140 °C oil bath and the reaction mixture was stirred and monitored by GC. After the reaction was complete, the reaction mixture was passed through a short plug of silica gel and washed with copious amount of Et_2O. The washings were concentrated and purified by flash chromatography on silica gel to offer the product. The products were identified by ^{1}H NMR.

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References and notes

1. (a) Amatore, C.; Jutand, A. *Acc. Chem. Res.* **2000**, *33*, 314–321. (b) Beletskaya, I. P.; Cheprakov, A. V. *Chem. Rev.* **2000**, *100*, 3009–3066. (c) Cabri, W.; Candiani, I. *Acc. Chem. Res.* **1995**, *28*, 2–7.
2. (a) Guillou, C.; Beunard, J.-L.; Gras, E.; Thal, C. *Angew. Chem., Int. Ed.* **2001**, *40*, 4745–4746. (b) Oestreich, M.; Dennison, P. R.; Kodanko, J. J.; Overman, L. E. *Angew. Chem., Int. Ed.* **2001**, *40*, 1439–1442. (c) Ashimori, A.; Bachand, B.; Calter, M. A.; Govek, S. P.; Overman, L. E.; Poon, D. J. *J. Am. Chem. Soc.* **1998**, *120*, 6488–6499. (d) Shibasaki, M.; Boden, C. J. D.; Kojima, A. *Tetrahedron* **1997**, *53*, 7371–7395. (e) de Meijere, A.; Meyer, F. E. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2379–2411.
3. (a) Fu, G. C.; Nguyen, S. T.; Grubbs, R. H. *J. Am. Chem. Soc.* **1993**, *115*, 9856–9857. (b) Nguyen, S. T.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1993**, *115*, 9858–9859. (c) Kubas, G. J. *Acc. Chem. Res.* **1988**, *21*, 120–128. (d) Gonzales, A. A.; Mukerjee, S. L.; Chou, S. J.; Zhang, K.; Hoff, C. D. J. *J. Am. Chem. Soc.* **1988**, *110*, 4419–4421.
4. Littke, A. F.; Fu, G. C. *J. Org. Chem.* **1999**, *64*, 10–11.
5. (a) Littke, A. F.; Fu, G. C. *J. Am. Chem. Soc.* **2001**, *123*, 6989–7000. (b) Shaughnessy, K. H.; Kim, P.; Hartwig, J. F. *J. Am. Chem. Soc.* **1999**, *121*, 2123–2132. (c) Stambuli, J. P.; Stauffer, S. R.; Shaughnessy, K. H.; Hartwig, J. F. *J. Am. Chem. Soc.* **2001**, *123*, 2677–2678. (d) Ehrentraut, A.; Zapf, A.; Beller, M. *Synlett* **2000**, 1589–1592.
6. (a) Ben-David, Y.; Portnoy, M.; Gozin, M.; Milstein, D. *Organometallics* **1992**, *11*, 1995–1996. (b) Portnoy, M.; Milstein, D. *Organometallics* **1993**, *12*, 1655–1664. (c) Portnoy, M.; Ben-David, Y.; Milstein, D. *Organometallics* **1993**, *12*, 4734–4735. (d) Portnoy, M.; Ben-Dvid, Y.; Rousso, I.; Milstein, D. *Organometallics* **1994**, *13*, 3465–3479. (e) Shaw, B. L.; Perera, S. D. *Chem. Commun.* **1998**, 1863–1864.
7. For recent reviews on palladacycles for Heck reactions, see (a) Dupont, J.; Pfeffer, M.; Spencer, J. *Eur. J. Inorg. Chem.* **2001**, 1917–1927. (b) Benford, R. B. *Chem. Commun.* **2003**, 1787–1796.
8. For the use of tetraphenylphosphonium salts in Heck reactions,

see: Reetz, M. T.; Lohmer, G.; Schwickardi, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 481–483.

9. (a) Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1290–1309. (b) Herrmann, W. A.; Weskamp, T.; Böhm, V. P. W. *Adv. Organomet. Chem.* **2002**, *48*, 1–69. (c) Jafarpour, L.; Nolan, S. P. *Adv. Organomet. Chem.* **2001**, *46*, 181–222. (d) Bourissou, D.; Guerret, O.; Gabbaï, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39–91. (e) Herrmann, W. A.; Köcher, C. *Angew. Chem., Int. Ed.* **1997**, *36*, 2162–2187.
10. Huang, J.; Schanz, H.-J.; Stevens, E. D.; Nolan, S. P. *Organometallics* **1999**, *18*, 2370–2375.
11. Schwarz, J.; Böhm, V. P. W.; Gardiner, M. G.; Grosche, M.; Herrmann, W. A.; Hieringer, W.; Raudaschl-Sieber, G. *Chem. Eur. J.* **2000**, *6*, 1773–1780.
12. Herrmann, W. A.; Elison, M.; Fischer, J.; Artus, G. R. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2371–2374.
13. (a) Liu, J.; Zhao, Y.; Zhou, Y.; Li, L.; Zhang, T. Y.; Zhang, H. *Org. Biomol. Chem.* **2003**, *1*, 3227–3231. (b) Pytkowicz, J.; Roland, S.; Mangeney, P.; Meyer, G.; Jutand, A. *J. Organomet. Chem.* **2003**, *678*, 166–179. (c) Loch, J. A.; Albrecht, M.; Peris, E.; Mata, J.; Faller, J. W.; Crabtree, R. H. *Organometallics* **2002**, *21*, 700–706. (d) Cesar, V.; Bellemin-Laponnaz, S.; Gade, L. H. *Organometallics* **2002**, *21*, 5204–5208. (e) Selvakumar, K.; Zapf, A.; Beller, M. *Org. Lett.* **2002**, *4*, 3031–3033. (f) Andrus, M. B.; Song, C.; Zhang, J. *Org. Lett.* **2002**, *4*, 2079–2082. (g) Magill, A. M.; McGuinness, D. S.; Cavell, K. J.; Britovsek, G. J. P.; Gibson, V. C.; White, A. J. P.; Williams, D. J.; White, A. H.; Skelton, B. W. *J. Organomet. Chem.* **2001**, *617*, 546–560. (h) Yang, C.; Lee, H. M.; Nolan, S. P. *Org. Lett.* **2001**, *3*, 1511–1514. (i) Grundemamm, S.; Albrecht, M.; Loch, J. A.; Faller, J. W.; Crabtree, R. H. *Organometallics* **2001**, *20*, 5485–5488. (j) Peris, E.; Loch, J. A.; Mata, J.; Crabtree, R. H. *Chem. Commun.* **2001**, 201–202. (k) McGuinness, D. S.; Cavell, K. J. *Organometallics* **2000**, *19*, 741–748. (l) Clyne, D. S.; Jin, J.; Genest, E.; Gallucci, J. C.; RajanBabu, T. V. *Org. Lett.* **2000**, *2*, 1125–1128. (m) Tulloch, A. A. D.; Danopoulos, A. A.; Tooze, R. P.; Cafferkey, S. M.; Kleinhenz, S.; Hursthouse, M. B. *Chem.Commun.* **2000**, 1247–1248.
14. (a) Seo, H.; Park, H.-J.; Kim, B. Y.; Lee, J. H.; Son, S. U.; Chung, Y. K. *Organometallics* **2003**, *22*, 618–620. (b) Danopoulos, A. A.; Winston, S.; Gelbrich, T.; Hursthouse, M. B.; Tooze, R. P. *Chem. Commum.* **2002**, 482–483. (c) Yang, C.; Lee, H. M.; Nolan, S. P. *Org. Lett.* **2001**, *3*, 1511–1514. (d) Herrmann, W. A.; Köcher, G. L. J.; Artus, G. R. J. *Chem. Eur. J.* **1996**, *2*, 1627–1636. (e) Tsoureas, N.; Danopoulos, A. A.; Tulloch, A. A. D.; Light, M. E. *Organometallics* **2003**, *22*, 4750–4758.
15. Albert, K.; Gisdakis, P.; Rösch, N. *Organometallics* **1998**, *17*, 1608–1616.
16. For example, **11c**: ^{1}H NMR δ 8.00 (m, 1H, NCH), 7.95 (s, 1H, Ar-H), 7.63–7.16 (m, 15H, Ar-H), 6.82 (m, 1H, NCH), 6.68 (s, 1H, Ar-H), 5.31 (s, 2H, CH_2), 2.40 (m, 2H, CH), 1.32 (d, $J=6.0$ Hz, 6H, CH_3), 1.26 (d, $J=6.0$ Hz, 6H, CH_3); ^{31}P NMR δ 16.52 (s).
17. Herrmann, W. A.; Broßmer, C.; Öfele, K.; Beller, M.; Fischer, H. *J. Mol. Catal. A* **1995**, *103*, 133–146.
18. Yang, C.; Nolan, S. P. *Synlett* **2001**, *10*, 1539–1542.
19. Ley, S. V.; Ramario, C.; Gordon, R. S.; Holmes, A. B.; Morrison, A. J.; McConvey, I. F.; Shirley, I. M.; Smith, S. C.; Smith, M. D. *Chem. Commun.* **2002**, 1134–1135.
20. Andappan, M. M. S.; Nilsson, P.; Larhed, M. *Mol. Diversity* **2003**, *7*, 97–106.
21. Oil, ^{1}H NMR δ 7.64 (d, $J=15.8$ Hz, 1H, CHAr), 7.39 (s, 1H, Ar), 7.30 (s, 2H, Ar), 6.37 (d, $J=15.8$ Hz, 1H, $CHCO_2$), 4.14 (t, 6.8 Hz, 2H, CO_2CH_2), 1.62 (m, $J=6.8$ Hz, 6.8 Hz, 2H, CH_2CH_2), 1.37 (m, $J=6.8$, 7.5 Hz, 2H, CH_2CH_3), 1.26 (s, 18H, $C(CH_3)_3$), 0.89 (t, $J=7.5$ Hz, 3H, CH_2CH_3).
22. Oil, ^{1}H NMR δ 7.58 (d, $J=15.8$ Hz, 1H, CHAr), 7.20 (s, 2H, Ar), 6.33 (d, $J=15.8$ Hz, 1H, $CHCO_2$), 4.19 (t, 6.8 Hz, 2H, CO_2CH_2), 3.73 (s, 3H, OCH_3), 2.29 (s, 6H, CH_3), 1.68 (m, $J=$ 6.8, 6.8 Hz, 2H, CH_2CH_2), 1.43 (m, $J=6.8$, 7.5 Hz, 2H, CH_2CH_3), 0.96 (t, $J=7.5$ Hz, 3H, CH_2CH_3).
23. Feuerstein, M.; Doucet, H.; Santelli, M. *Synlett* **2001**, *12*, 1980–1982.
24. Lewis, F. D.; Oxman, J. D.; Gibson, L. L.; Hampsch, H. L.; Quillen, S. L. *J. Am. Chem. Soc.* **1986**, *108*, 3005–3015.
25. Feuerstein, M.; Doucet, H.; Santelli, M. *J. Org. Chem.* **2001**, *66*, 5923–5925.
26. Terrian, D. L.; Mohammad, T.; Morrison, H. *J. Org. Chem.* **1995**, *60*, 1981–1984.
27. Murai, M.; Hashimoto, H.; Itoh, K.; Nomura, M. *J. Chem. Soc., Perkin Trans. 1* **1990**, 2207–2211.
28. Ceccon, A.; Crociani, L.; Santi, S.; Venzo, A.; Biffis, A.; Boccaletti, G. *Tetrahedron Lett.* **2002**, *43*, 8475–8478.
29. Oil, ^{1}H NMR δ 10.05 (s, 1H, CHO), 8.03 (s, 1H, Ar), 7.89 (d, $J=7.5$ Hz, 1H, Ar), 7.78 (d, $J=7.5$ Hz, 1H, Ar), 7.73 (d, $J=15.8$ Hz, 1H, CHAr), 7.58 (t, $J=7.5$ Hz, 1H, Ar), 7.54 (d, $J=15.8$ Hz, 1H, $CHCO_2$), 4.23 (t, $J=6.8$ Hz, 2H, CO_2CH_2), 1.70 (m, $J=6.8$, 6.8 Hz, 2H, CH_2CH_2), 1.45 (m, $J=6.8$, 7.5 Hz, 2H, CH_2CH_3), 0.98 (t, $J=7.5$ Hz, 3H, CH_2CH_3).
30. Calo, V.; Nacci, A.; Monopoli, A.; Lopez, L.; di Cosmo, A. *Tetrahedron* **2001**, *57*, 6071–6077.
31. Herrmann, W. A.; Böhm, V. P. W.; Gstöttmayr, C. W. K. *J. Organomet. Chem.* **2001**, *617*, 616–628.
32. (a) Mikroyannidis, J. A. *Macromolecules* **2002**, *35*, 9289–9295. (b) Kim, J. H.; Lee, H. *Chem. Mater.* **2002**, *14*, 2270–2275. (c) Shim, H. K.; Ahn, T.; Lee, H. Y.; Lee, J. I. *Korea Polym. J.* **2001**, *9*, 116–121. (d) Liu, Y. B.; Lahti, P. M.; La, F. *Polymer* **1998**, *39*, 5241–5244.
33. Andrus, M. B.; Song, C.; Zhang, J. *Org. Lett.* **2002**, *4*, 2079–2082.
34. Spencer, A. *J. Organomet. Chem.* **1983**, *247*, 117–122.
35. Engler, T. A.; Gfesser, G. A.; Draney, B. W. *J. Org. Chem.* **1995**, *60*, 3700–3706.
36. Mp 188–191 °C, ^{1}H NMR δ 7.50 (s, 4H, Ar), 7.35 (d, $J=$ 7.5 Hz, 2H, Ar), 7.11 (d, $J=7.5$ Hz, 2H, Ar), 7.08 (d, $J=$ 16.6 Hz, 1H, $CH{=}CH$), 6.98 (d, $J=16.6$ Hz, 1H, $CH{=}CH$), 2.29 (s, 3H, CH_3).
37. Mp 178–180 °C, 1H NMR δ 7.76–7.64 (m, 5H, Ar), 7.40–7.33 (m, 4H, Ar), 7.16–7.10 (m, 4H, Ar, $CH{=}CH$), 2.29 (s, 3H, CH_3).
38. Mp 205–207 °C, 1H NMR δ 7.44–7.39 (m, 4H, Ar), 7.32–7.30 (m, 2H, Ar), 7.17 (d, $J=7.5$ Hz, 2H, Ar), 7.06 (d, $J=15.8$ Hz, 1H, $CH{=}CH$), 6.99 (d, $J=15.8$ Hz, 1H, $CH{=}CH$), 2.36 (s, 3H, CH_3).
39. Mallory, F. B.; Mallory, C. W. *J. Org. Chem.* **1983**, *48*, 526–532.
40. Takahashi, Y.; Ito, T.; Sakai, S.; Ishii, Y. *Chem. Commun.* **1970**, 1065–1066.