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Novel triphenylarsinyl-functionalized *N*-heterocyclic carbene ligands in palladium-catalyzed C–C coupling reactions ☆

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ABSTRACT

Synthesis of novel triphenylarsinyl-functionalized *N*-heterocyclic carbene pre-ligands starting from *N,N*-dimethylbenzylamine, chlorodiphenylarsine and different 1-substituted imidazoles and their characterization by NMR and X-ray analysis is reported. Furthermore, these precursors are applied to different palladium-catalyzed reactions such as Heck-, hydro-Heck, π, σ domino-Heck and Suzuki reactions to give the C–C coupling products in good to excellent isolated yields.

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1. Introduction

Since Arduengo succeeded in the generation of stable imidazol-2-ylidenes [1], cyclic, electron-rich carbenes have gained increasing importance as ligands in homogenous catalysis [2] with transition metals such as Ni [3], Cu [4] or Pd [5]. In comparison to standard phosphines carbenes as ligands in transition metal complexes often show higher stability towards oxygen and temperature and less sensitivity to moisture [2]. Additionally, a ligand excess is not required [2]. Carbene palladium complexes have already been applied to Heck and Suzuki reactions [6], successfully. Several bridged bis-imidazolium salts are known as chelating carbene pre-ligands in Heck reactions (see Scheme 1).

Herrmann [7] et al. were able to generate palladium complexes **1** and to identify the chelating ligand by X-ray analysis as well as the Douthwaite [8] group. Danopoulos [9a,b], Lee [10] and Zhou [11] went a step further. They combined the properties of carbenes with the ones of phosphines and synthesized chelating carbene phosphine pre-ligands of the types shown in Scheme 2.

X-ray analyses of type **2** salts have been published by Labande and Poli [9c]. In all cases generation of the carbene was achieved by deprotonation of the corresponding salts. Lee [10] trapped the free carbene of type **2** as a palladium complex and reported its X-ray structure. Neither X-ray analyses of the salts of type **3** nor their Pd-complexes have been reported yet, though.

The use of arsine ligands has proved especially advantageous [12] in Pd-catalyzed C–C coupling reactions, due to their high reactivity and selectivity as well as their high stability towards air in comparison to the structurally analogous phosphines [13]. Therefore, we decided to substitute phosphorus by arsenic in chelating carbene complexes of type **3**.

2. Results and discussion

2.1. X-ray analysis of 3-(2-(diphenyl-phosphinyl)benzyl)-1-phenyl-1H-imidazol-3-ium chloride (**3a**)

For homogenous catalysis it appeared desirable to learn to know and compare the geometric parameters of mixed carbene phosphine and arsine ligands of type **3** by means of X-ray analyses. Therefore, we first synthesized salt **3a** (Ar = Ph) by the procedure published by Zhou [11]. Recrystallisation from a mixture of acetonitrile and dichloromethane gave single crystals suitable for X-ray crystallography.

Compound **3a** crystallizes in the triclinic space group $P\bar{1}$ (No. 2) with two formula units in the unit cell. The crystal structure is characterized by discrete 3-(2-(diphenyl-phosphinyl)benzyl)-1-phenyl-1*H*-imidazol-3-ium cations, chloride anions and water molecules, which are involved in hydrogen bonds (Fig. 2).

A view of the cation is shown in Fig. 1, the relevant bond lengths and angles are listed in Table 2. The three aromatic rings are

☆ Palladium-catalyzed reactions part 6; For part 5 see Ref. [12a].

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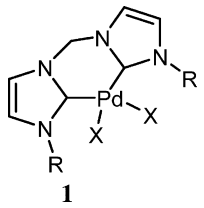

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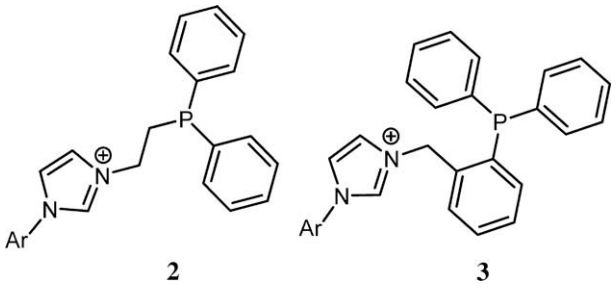
Scheme 1. Palladium-carbene-complexes **1**.



2 3

Scheme 2. Imidazolium salts **2** and **3** of mixed carbene phosphine ligands.

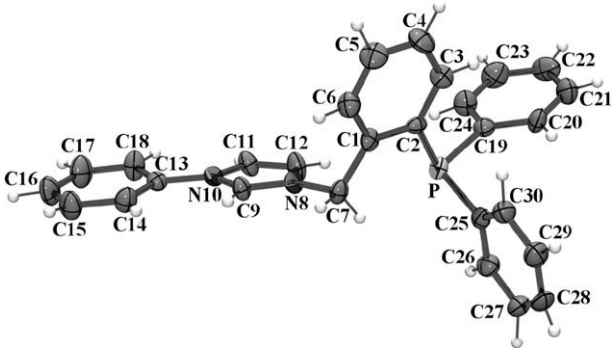


Fig. 1. X-ray crystal structure of **3a**.

attached to the phosphorus atom in a propeller-like conformation. The $P(C_6H_5)_3$ moiety of this cation exhibits a C_3 symmetry with torsion angles C(1)–C(2)–P–C(25) 86.32(2), C(20)–C(19)–P–C(2) 99.79(3) and C(30)–C(25)–P–C(19) 88.41(1)°. The P–C bond lengths range from 181.8(1) to 183.9(1) pm, and C–P–C angles from 102.43(1) to 104.30(2)° (Table 2). Each Cl^- anion is connected via hydrogen bonds to water molecules. The intermolecular O···Cl distances between the oxygen atoms of water molecules and the chloride anions range from 321.2(1) to 3.300(1) pm and the O–H···Cl angles from 169.1(1) to 174.6(1)°.

The distance between the carbene precursor carbon and the phosphorus atom is 5.119 Å. The packing of the unit cell is dominated by the π-stacking of the aromatic rings on the one hand and on the other hand by the alteration of layered imidazolium units including their counterion chloride.

2.2. Synthesis of three novel triphenyl-arsinyl-functionalized imidazolium salts

The starting material chlorodiphenylarsine, unlike its phosphine analog, is commercially not available. But it can be synthesized in a safety-apparatus following a procedure by Kauffmann [14] et al. Arsenic oxide is used as arsenic source. This oxide is easily converted into arsenic acid by addition of water. Under catalytic reduction conditions arsenic acid can react with phenylhydrazine in the presence of copper(I) oxide to give after addition of hydrochloric acid the desired chlorodiphenylarsine **4** (see Scheme 3).

After *ortho*-lithiation of *N,N*-dimethylbenzylamine (**5**) molecule **4** is added to give *o*-(diphenylarsinyl)-*N,N*-dimethylbenzylamine (**6**) in 77% isolated yield. This novel amine **6** is converted under reflux conditions in the presence of chloroethyl formate into the key intermediate *o*-(diphenylarsinyl)benzyl chloride (**7**) in 76% yield (see Scheme 4).

This key intermediate **7** is converted into 3-(2-(diphenylarsinyl)benzyl)-1-phenyl-1*H*-imidazol-3-ium chloride (**11**), 3-(2-(diphenylarsinyl)benzyl)-1-mesityl-1*H*-imidazol-3-ium chloride (**12**) and 1-*tert*-butyl-3-(2-(diphenylarsinyl)benzyl)-1*H*-imidazol-3-ium chloride (**13**) by adding the commercially available 1-phenylimidazole (**8**) or 1-mesitylimidazole (**9**) and *t*-butylimidazole (**10**) under reflux conditions in ethanol. The latter are synthesized

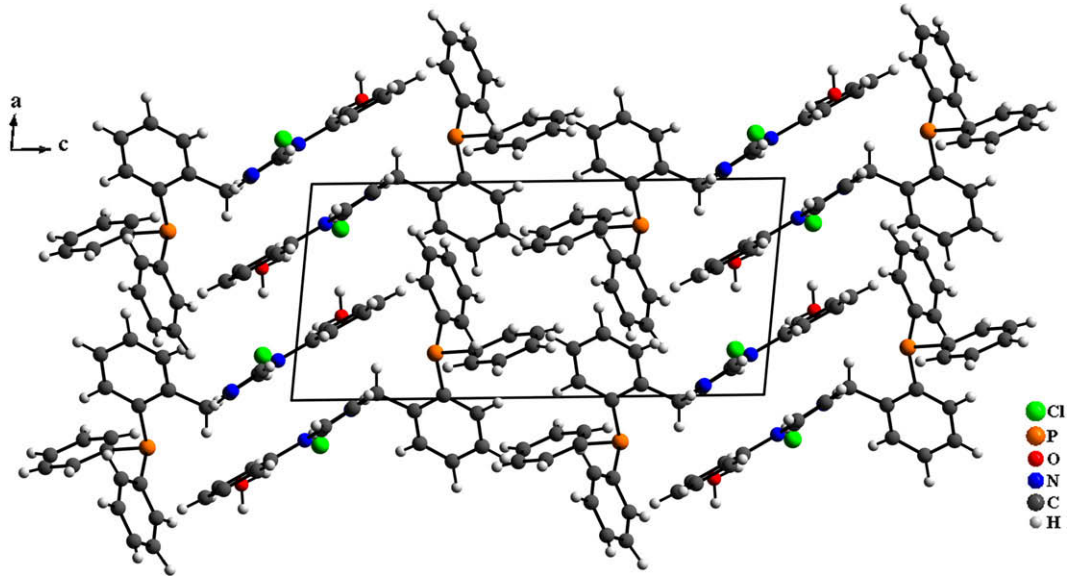


Fig. 2. Packing of unit cell of **3a** along axis *b*.

Table 1
Yield of the imidazolium salts **11**–**13**

R	Yield (%)	Product
Phenyl	77	**11**
Mesityl	53	**12**
t-Butyl	82	**13**

by a one-pot procedure [15] starting from either mesitylamine or *t*-butylamine.

The resulting novel triphenyl-functionalized imidazolium salts are obtained in moderate to good isolated yields (see Table 1). A side product, (2-(ethoxymethyl)phenyl)diphenylarsine (**14**), was also isolated resulting from a slow reaction between the key intermediate **7** and the solvent ethanol (see Scheme 5).

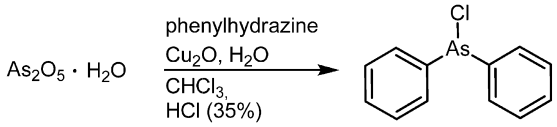
In addition to the usual characterization of these novel compounds by NMR-techniques molecule **11** was recrystallized from methanol to give a single crystal. X-ray analysis of 3-(2-(diphenylarsinyl)-benzyl)-1-phenyl-1*H*-imidazol-3-ium chloride (**11**) proved the proposed structure.

Compound **11** crystallizes in the monoclinic space group $P2_1/c$ (No. 14) with four formula units in the unit cell. The crystal structure is not isotypic with **3a** and is characterized by discrete 3-(2-(diphenylphosphinyl)benzyl)-1-phenyl-1*H*-imidazol-3-ium cations, chloride anions and water molecules, which are involved in hydrogen bonds (Fig. 4).

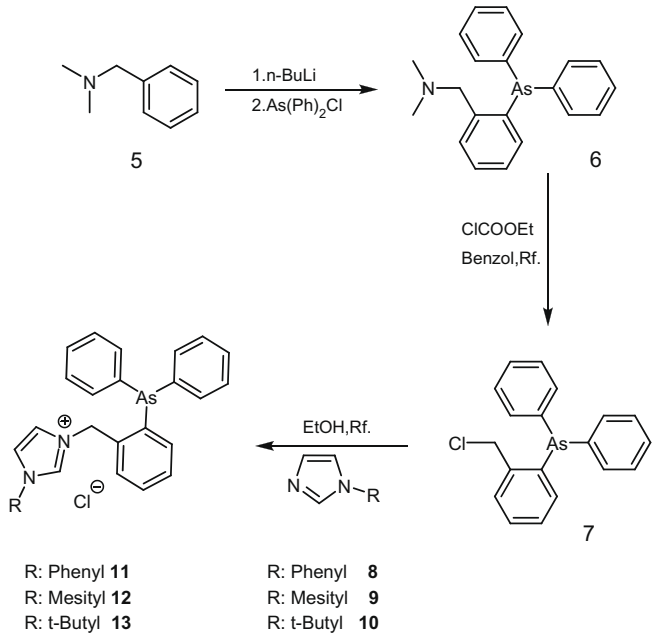
The $As(C_6H_5)_3$ moiety of this cation exhibits also C_3 symmetry with torsion angles C(1)–C(2)–As–C(19) 107.43(2), C(20)–C(19)–As–C(25) 96.71(2) and C(30)–C(25)–As–C(2) 80.48(1)°.

Table 2
Selected bond lengths (pm) and bond angles (°)

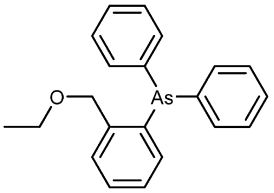
Compound **3a**	
P–C(2)	183.6(1)
P–C(19)	181.8(1)
P–C(25)	183.9(1)
C(1)–C(7)	151.8(1)
C(7)–N(8)	147.9(1)
C(9)–N(8)	134.4(1)
C(9)–N(10)	134.7(1)
C(11)–N(10)	138.7(1)
C(11)–C(12)	133.7(1)
C(12)–N(8)	136.6(1)
C(2)–P–C(19)	102.84(1)
C(2)–P–C(25)	102.43(1)
C(19)–P–C(25)	104.30(1)
Compound **11**	
As–C(2)	197.9(1)
As–C(19)	195.9(1)
As–C(25)	198.2(1)
C(1)–C(7)	150.7(1)
C(7)–N(8)	148.4(1)
C(9)–N(8)	133.1(1)
C(9)–N(10)	135.1(1)
C(11)–N(10)	139.2(1)
C(11)–C(12)	130.0(1)
C(12)–N(8)	138.1(1)
C(2)–As–C(19)	101.64(1)
C(2)–As–C(25)	98.94(1)
C(19)–As–C(25)	98.02(1)



Scheme 3. Preparation of chlorodiphenylarsine (**4**).



Scheme 4. Synthetic route to the novel imidazolium salts **11**–**13**.



Scheme 5. S_N-reaction side product **14** of **7**.

These values are comparable with those in compound **3a**. The As–C bond lengths range from 195.9(1) to 198.2(1) pm, and C–As–C angles from 98.02(1) to 101.64(2) (Fig. 3 and Table 2). The 3-(2-(diphenylarsinyl)benzyl)-1-phenyl-1*H*-imidazol-3-ium cations and water molecules form layers, which alternate with layers of chloride anions. They are linked by hydrogen bonds between the Cl^- anions and water molecules. The intermolecular O···Cl distances range from 323.9(1) to 328.4(1) pm and the O–H···Cl angles from 167.3(1) to 173.5(1)°.

The carbon on which the carbene will be generated later is 3.539 Å away from the arsine atom.

With these novel triphenylarsinyl-functionalized imidazolium salts **11–13** in hand their catalytic properties were investigated in Heck-, hydro-Heck- (Heck reaction under reductive conditions), π, σ domino-Heck and Suzuki reactions.

First, the standard Heck reaction on butyl acrylate (**15**) was performed under mild conditions at 60–65 °C (see Scheme 6).

Under these conditions with three different As-ligands the Heck-product (*E*)-butyl-3-*p*-tolyl acrylate (**16**) was obtained in excellent yields. In comparison to the results from Zhou [11], who used the phosphine analogue of **11**, we needed less Pd and ligand and could work at 60–65 °C, in order to obtain almost quantitative yields (see Table 3). After these encouraging results we applied these ligands to the hydro-Heck reaction on norbornene (**17**) to give 2-*exo*-phenylnorbornane (**18**). Kaufmann and Schäffner [16] had already used 1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride as carbene source for this hydrophenylation and obtained the product in 94% yield. Recently, Zhou [17] reported the application of their phosphine-NHC-ligands to this hydroarylation reaction (see Scheme 7 and Table 4).

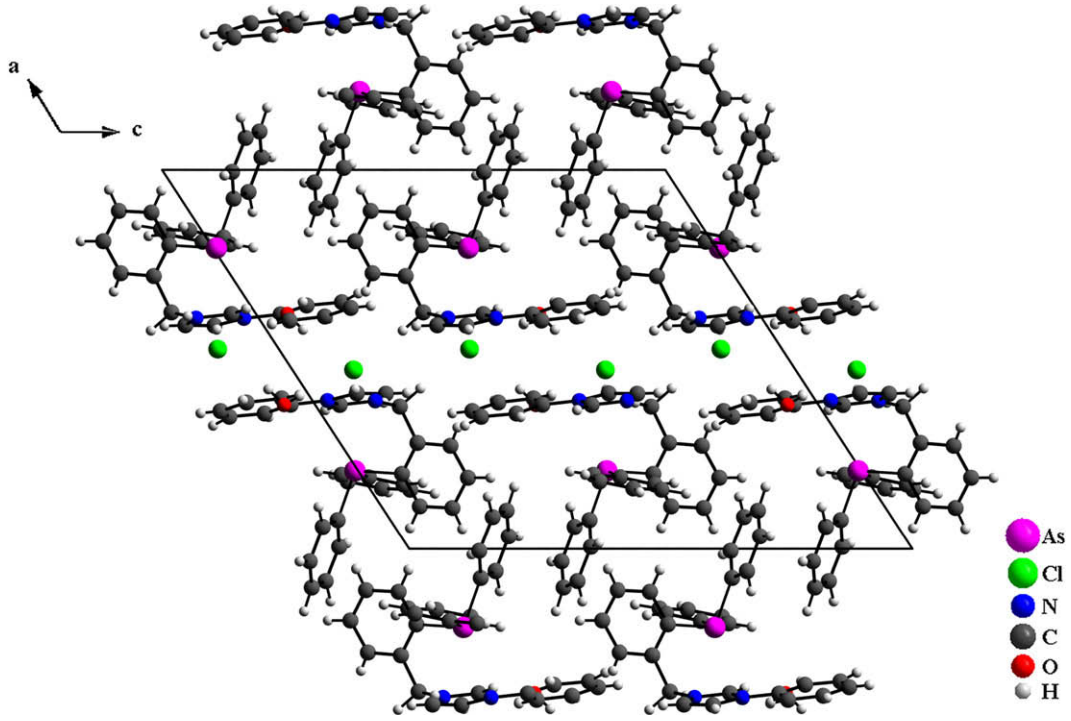


Fig. 4. Layer structure of **11** along axis *b*.

The novel mixed carbene arsine ligand precursors **11** and **12** were also successfully applied to this type of C–C coupling reaction. The hydrophenylation product **18** could be isolated in very good yields (81–86%) (see Table 4).

In 2005 Kaufmann [18] et al. discovered the first example of a π,σ domino-Heck rearrangement on bishomobarrelene (**19**) catalyzed by an *in situ* generated catalyst of $As(Ph)_3$ and $Pd(OAc)_2$ (see Scheme 8 and Table 5).

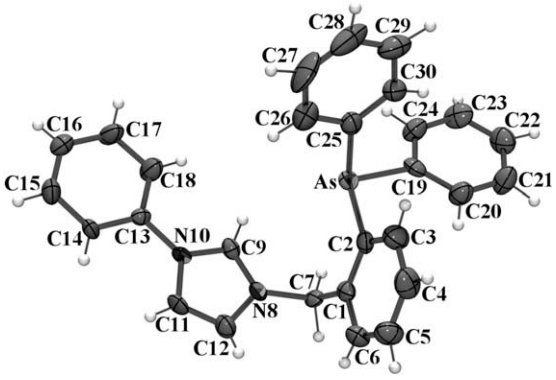
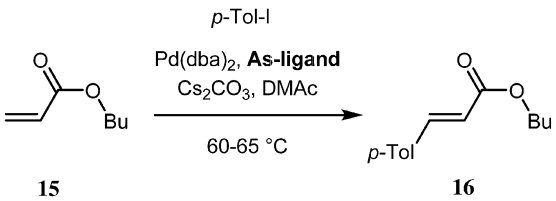


Fig. 3. X-ray crystal structure of **11**.

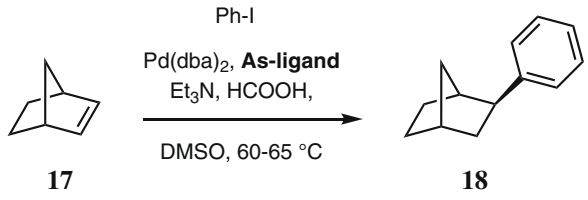


Scheme 6. Heck-arylation of butyl acrylate **15**.

These combined carbene arsine pre-catalysts **11** and **12** catalyzed this rearrangement in moderate yields, too. It is remarkable that the sterically more hindered molecule **12** gives the higher yield compared to **11**. It is worth mentioning, that without the reducing agent HCOOH the rearrangement takes place only when using the mesityl-compound **12**. Apparently, the three methyl groups are necessary to form a catalytically more active species.

In 2004 Zhou [19] et al. applied their phosphine-imidazolium system to the Suzuki cross coupling reaction. In contrast to their conditions we used DMAc as solvent at lower temperature (65 °C) in order to test the novel arsine containing compounds **11** and **12** in the Suzuki reaction (see Scheme 9 and Table 6).

The *p*-methylbiphenyls were obtained in good to excellent yields by using pre-catalyst **11** and **12**. These yields are as good or even better than the one obtained with $As(Ph)_3$. Even the steri-



Scheme 7. Hydro-Heck reaction on norbornene (**17**).

Table 3
Ligand variation in the Heck reaction of butyl acrylate **15**–**16**

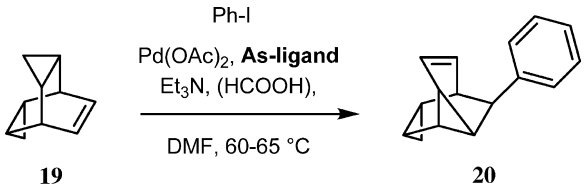
As-ligand	Time (h)	Yield (%)
11	20	99
12	20	99
13	20	100

0.66 mol% $Pd(dba)_2$, 0.66 mol% As-ligand, 1.5 mmol butyl acrylate, 2 equiv. base, 2.25 equiv. *p*-iodotoluene.

Table 4
Ligand variation in the hydro-Heck reaction of **17**–**18**

As-ligand	Time (h)	Yield (%)
11	22	86
12	22	81

2.5 mol% $Pd(dba)_2$, 11 mol% As-ligand, 2 mmol norbornene, 3.5 equiv. base, 2 equiv. iodobenzene, 3 equiv. formic acid.

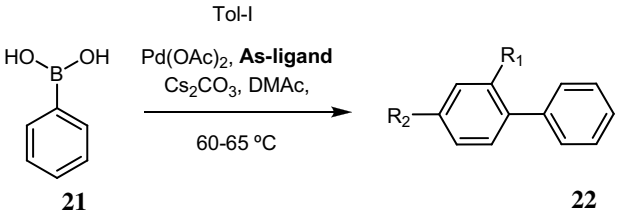


Scheme 8. π,σ domino-Heck rearrangement.

Table 5
Ligand variation in the π,σ domino-Heck rearrangement of **19**

As-ligand	HCOOH	Time (h)	Yield (%)
11	+	19	43
12	+	19	48
11	–	14	0
12	–	19	44

2.5 mol% $Pd(OAc)_2$, 11 mol% As-ligand, 2 mmol bishomobarrelene, 4 equiv. base, 1.5 equiv. iodobenzene, 3 equiv. formic acid.



Scheme 9. Suzuki-coupling of **21** to methyl-biphenyls of type **22**.

Table 6
Ligand variation in the Suzuki reaction of phenylboronic acid **21**

As-ligand	Tol-I	R_1/R_2	Time (h)	Yield (%)
11	*p*-Tol-I	H/Me	19	99
12	*p*-Tol-I	H/Me	19	87
$As(Ph)_3$	*p*-Tol-I	H/Me	19	91
11	*o*-Tol-I	Me/H	19	88
12	*o*-Tol-I	Me/H	19	93

0.5 mol% $Pd(OAc)_2$, 0.5 mol% As-ligand, 1.5 mmol phenyl boronic acid, 2 equiv. base, 1 equiv. iodotoluene.

cally more hindered *o*-tolyl iodide can be coupled with phenyl boronic acid (**21**) in very good yields.

3. Conclusion

In summary, we have synthesized novel arsine-imidazolium salts and characterized them by NMR and X-ray techniques. These salts are highly efficient pre-catalysts and can be used in various palladium-catalyzed reactions such as Heck, hydro-Heck, π,σ domino-Heck and Suzuki reactions.

4. Experimental

All reactions were carried out in oven-dried flasks and Schlenk-tubes under nitrogen atmosphere. NMR data were recorded on a Bruker Avance DPX 200 (^{1}H: 200 MHz, ^{13}C: 50 MHz) and Bruker Avance 400 spectrometer (^{1}H: 400 MHz, ^{13}C: 100 MHz) with TMS as internal standard. δ values are given in ppm; *J* values in Hz. Multiplicities of ^{13}C NMR signals were detected by DEPT-135-method and reported as follows: + for CH or CH_3, – for CH_2 and C_{quat} for C. Mass spectra were obtained with a Varian Saturn 2100T or Hewlett-Packard MS LC/MSD Series 1100 MSD; high resolution mass spectra were recorded with a Finnigan MAT95 (EI) and Bruker Daltonik Apex IV (ESI); molecular peak ion matching at $R \approx 10000$ to be within ±2 ppm. CHN-analyses were performed on a Carlo Erba Instrumentazione Elemental Analyzer 1106. Melting points are uncorrected. Solvents were dried by standard procedures. Flash chromatography was performed on Merck silica gel 60 (40–63 μm) with distilled solvents. Given yields are isolated yields. X-Ray-analysis was done on a single crystal diffractometer STOE IPDS II with cryostream Cooler 700 (Oxford Cryosystems).

4.1. 3-(2-(Diphenylphosphinyl)benzyl)-1-phenyl-1H-imidazol-3-ium chloride (**3a**)

Synthesis of **3a** refers to literature [11].

Crystal data: $C_{28}H_{26}PClN_2O$ (**3a**): see Table 7. A suitable single crystal of the title compound was selected under a polarization microscope and mounted in a glass capillary. The crystal structure was determined by X-ray diffraction analysis using graphite monochromated Mo K_α radiation (0.71073 Å), whereas the scattering intensities were collected with a single crystal diffractometer (STOE IPDS II). The crystal structure was solved by Direct Methods using SHELXS-97 [20] and refined using alternating cycles of least squares refinements against F^2 (SHELXL-97) [20]. All non-H atoms were located in difference Fourier maps and were refined with anisotropic displacement parameters. The H positions were determined by a final difference Fourier synthesis. For the presentation

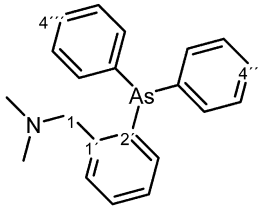
Table 7
Crystallographic data for compound **3a**

Formula	$C_{28}H_{26}N_2OPCl$
Formula weight (g/mol)	473.92
Colour/habit	Colourless/block
Crystal size (mm)	0.30 × 0.28 × 0.27
Crystal system	Triclinic
Space group	*P*1 (no. 2)
a (Å)	9.113(2)
b (Å)	9.099(2)
c (Å)	17.257(4)
α (°)	86.23(2)
β (°)	82.84(2)
γ (°)	60.11(2)
V (Å^3)	1231.0(5)
Z	2
T (K)	223(2)
μ (mm^{-1})	0.243
θ Range (°)	0.988–25.00
Index ranges (*h*, *k*, *l*)	±10, ±10, ±20
Measured reflections	13158
Independent reflections	4280
R_{int}	0.1044
Reflections with [$I > 2\sigma(I)$]	8878
Parameters	402
R_1 wR_2 [$I > 2\sigma(I)$][a]	0.0604/0.0838
R_1 wR_2 (all data)[a]	0.0832/0.1077
GOF (on F^2)[a]	1038
Largest difference peaks and hole (e A^{-3})	+0.491 and −0.303

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(|F_o|^2 - |F_c|^2)^2]/\Sigma [w(|F_o|^2)^2]\}^{1/2}$; GOF = $\{\Sigma [w(F^2_o - F^2_c)^2]/(n-p)\}^{1/2}$.

of the structure drawings the programs DIAMOND [21], ORTEP [22] and POV-RAY [23] were applied.

*4.2. o-(Diphenylarsinyl)-N,N-dimethylbenzylamine (**6**) [24]*



Under nitrogen atmosphere 30 mL (48.5 mmol) *n*-BuLi (1.6 M in hexane) were placed in a two-necked-flask. At room temperature 6.55 mL (43.5 mmol) *N,N*-dimethylbenzylamine (**5**) were slowly added. The mixture was diluted with 60 mL dry ether and subsequently allowed to stand over night without stirring. The resulting solid was suspended in the orange solution by violent stirring. Then 10.56 g (39.9 mmol) chlorodiphenylarsine (**4**) were added at −35 °C. The mixture was stirred over night by warming to room temperature. Fourteen milliliter water was added at 0 °C. The mixture was distributed between 100 mL of ether and 100 mL of HCl (2 N). The organic layer was separated and washed with 100 mL HCl (2 N). The combined acidic layers were brought to pH 12–13 by addition of 70 mL aqueous NaOH (6 N). This layer was extracted with 3 × 70 mL DCM. The combined organic phases were dried over $MgSO_4$, filtered and brought to dryness. After chromatography (SiO_2; PE:EE = 4:1) a yellow oil (11.14 g, 77%) was obtained.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.01 (s, 6 H, CH_3), 3.59 (s, 2 H, 1 H), 7.09 (dd, *J* = 7.5, 1.1 Hz, 1H, 5′-H), 7.20 (ddd, *J* = 7.2, 7.3, 1.7 Hz, 1 H, 4′-H), 7.29–7.38 (m, 12 H, $H_{arom.}$).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 44.1 (+, 2 C, CH_3), 63.9 (−, C-1), 127.3 (+, C-4′), 127.8 (+, 2 C, C-4″, C-4‴), 128.1 (+, C-3′), 128.3 (+, 4 C, C-3″, C-5″, C-3‴, C-5‴), 129.0 (+, C-6′), 133.7 (+, 4 C, C-2″, C-6″, C-2‴, C-6‴), 134.5 (+, C-5′), 140.5 ($C_{quat.}$, C-2′), 141.0 (2 $C_{quat.}$, C-1″, C-1‴), 143.8 ($C_{quat.}$, C-1′).

R_f = 0.61 (SiO_2, PE:EE = 1:1).

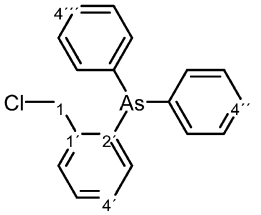
IR (NaCl): ***ν*** = 3051, 2972, 2940, 2853, 2815, 2777, 1952, 1878, 1816, 1740, 1580, 1481, 1454, 1434, 1361, 1305, 1269, 1249, 1204, 1175, 1147, 1117, 1095, 1074, 1025, 999, 971, 945, 945, 911, 876, 847, 737, 697, 665, 618, 475, 415, 405 cm^{-1}.

MS (DCP, 70 eV); *m*/*z* (%): 364 (10) [M^++H], 286 (100) [$M^+-C_6H_5$].

CHN: $C_{21}H_{22}AsN$: Calc. C 69.42, H 6.10, N 3.86. Found C 69.47, H 6.19, N 3.94%.

HRMS: $C_{21}H_{22}AsN$: Calc. 363.0968;
[M+H]$^+$ Calc. 364.10410. Found 364.10397.

*4.3. o-(Diphenylarsinyl)benzyl chloride (**7**)*



Under nitrogen atmosphere 2.9 mL (30.67 mmol) ethyl chloroformate was added to a solution of 11.14 g (30.67 mmol) *o*-(diphenylarsinyl)-*N,N*-dimethylbenzylamine (**7**) in 50 mL dry benzene. After heating for 5 h at reflux the solvent was evaporated. The yellow residue was purified by chromatography (SiO_2; PE:EE = 90:1) to give the colourless benzyl chloride (8.23 g, 76%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.81 (s, 2 H, 1-H), 7.07 (dd, *J* = 7.6, 1.4 Hz, 1 H, 5′-H), 7.21 (ddd, *J* = 7.5, 7.5, 1.4 Hz, 1 H, 4′-H), 7.28–7.37 (m, 11 H, 3′-H, 2″-H, 6′-H, 2‴-H, 6‴-H), 7.48 (dd, *J* = 7.6, 1.2 Hz, 1 H, 6′-H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 45.9 (−, C-1), 128.5 (+, 2 C, C-4″, C-4‴), 128.7 (+, 4 C, C-3″, C-5″, C-3‴, C-5‴), 128.9 (+, C-4′), 129.2 (+, C-3′), 129.9 (+, C-6′), 133.7 (+, 4 C, C-2″, C-6″, C-2‴, C-6‴), 134.5 (+, C-5′), 138.6 ($C_{quat.}$, C-1″, C-1‴), 139.5 ($C_{quat.}$, C-2′), 141.6 ($C_{quat.}$, C-1′).

R_f = 0.52 (SiO_2, PE:EE = 16:1).

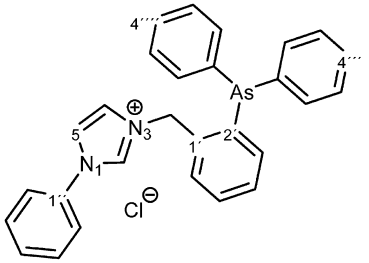
M.p. 82–83 °C (PE:EE).

IR (KBr): *ν* = 3048, 3001, 2963, 1959, 1825, 1650, 1575, 1478, 1464, 1431, 1306, 1260, 1204, 1184, 1153, 1114, 1067, 1021, 998, 951, 918, 819, 774, 739, 696, 674, 576, 501, 478, 466, 442 cm^{-1}.

MS (DCP, 70 eV); *m*/*z* (%): 354 (39) [M^+], 240 (67) [$M^+-C_6H_5$–Cl–2H], 227 (13) [$M^+-C_6H_5-CH_2Cl$], 200 (21) [M^+-$2C_6H_5$], 165 (100) [$M^+-2C_6H_5$-Cl], 77 (25) [$M^+-C_{13}H_{11}AsCl$].

CHN: $C_{19}H_{16}AsCl$: Calc. C 64.34, H 4.55, Cl 10.00. Found C 64.37, H 4.58, Cl 9.99%.

*4.4. 3-(2-(Diphenylarsinyl)benzyl)-1-phenyl-1H-imidazol-3-ium chloride (**11**)*



1.458 g (4.1 mmol) *o*-(Diphenylarsinyl)benzyl chloride (**7**) and 0.51 mL (4 mmol) 1-phenyl-imidazole (**8**) were dissolved in 16 mL dry ethanol under nitrogen atmosphere. After refluxing for 48 h the solvent was evaporated. The residue was purified by chromatography (SiO_2; DCM: MeOH = 8:1) to give the phenyl-imidazolium chloride (1.53 g, 77%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.96 (s, 2 H, CH_2), 7.05 (dd, *J* = 1.2, 7.6 Hz, 1 H, 3′-H), 7.16–7.20 (m, 5 H, 4-H, 5′-H, $H_{arom.}$), 7.24–7.34 (m, 7 H, 4′-H, 4″-H, $H_{arom.}$), 7.40–7.45 (m, 2 H, 4‴-H, 4-⁗H), 7.46–7.52 (m, 2 H, 3″-H, 5″-H), 7.65 (dd, *J* = 1.9, 1.9 Hz, 1 H, 5-H), 7.68–7.72 (m, 2 H, 2″-H, 6″-H), 7.90 (d, *J* = 7.6 Hz, 1 H, 6′-H), 11.08 (s, 1 H, 2-H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 52.8 (−, CH_2), 120.2 (+, C-5), 121.3 (+, $C_{arom.}$), 121.4 (+, 2 C, C-2″, C-6″), 122.1 (+, C-4), 128.8 (+, $C_{arom.}$), 128.9 (+, $C_{arom.}$), 129.8 (+, $C_{arom.}$), 130.0 (+, C-5″, C-3″), 130.2 (+, $C_{arom.}$), 131.8 (+, C-6′), 133.5 (+, C-5′), 134.1 ($C_{quat.}$, C-1″), 134.6 (+, C-3′), 136.0 (+, C-2), 136.8 ($C_{quat.}$, C-1′), 136.9 ($C_{quat.}$, C-1‴, C-1⁗), 139.9 ($C_{quat.}$, C-2′).

R_f = 0.33 (SiO_2, DCM:MeOH = 5:1).

M.p. 186–188 °C (DCM/MeOH).

IR (KBr): *ν* = 3386, 3049, 1597, 1550, 1496, 1480, 1433, 1374, 1305, 1263, 1211, 1186, 1121, 1072, 1023, 998, 914, 830, 738, 695, 623, 521, 470 cm^{-1}.

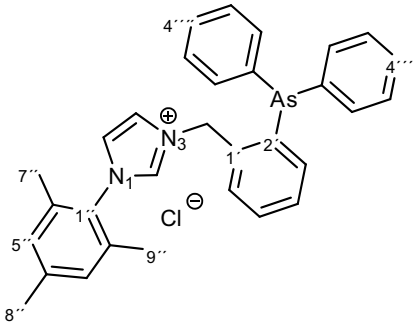
MS (ESI); *m*/*z* (%): 463 (100) [M−Cl]$^+$, 464 (34) [M−Cl+H]$^+$.

HRMS: $C_{28}H_{24}AsClN_2$: Calc. 498.0844;

$[M-Cl]^+$: Calc. 463.11500. Found 463.11506.

Crystal data: $C_{28}H_{26}AsClN_2O$ (**11**): see Table 8. The X-ray diffraction data were collected on a STOE IPDS diffractometer with Mo K_α radiation. The structures were dissolved by direct methods using SHELXS-97 [20] and refined using alternating cycles of least squares refinements against F^2 (SHELXL-97)[20]. All non H atoms were found in difference Fourier maps and were refined with anisotropic displacement parameters. The H positions were determined by final difference Fourier syntheses. For preparation of the structure drawings the programs DIAMOND [21], ORTEP [22] and POV-RAY™ [23] were used.

4.5. 3-(2-(Diphenylarsinyl)benzyl)-1-mesityl-1H-imidazol-3-ium chloride (*12*)



The procedure is the same as in **11** except for exchanging phenyl-imidazole (**8**) by mesityl-imidazole (**9**). The product was purified by chromatography (SiO_2; DCM:MeOH = 8:1) to give the mesityl-imidazolium chloride (1.53 g, 77%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.00 (s, 6 H, 7″-H, 9″-H), 2.32 (s, 3 H, 8″-H), 6.08 (s, 2 H, CH_2), 6.97 (s, 2 H, 5″-H, 3″-H), 7.07 (dd, J = 1.8 Hz, 1 H, 5′-H), 7.09 (dd, J = 7.6, 1.2 Hz, 1 H, 4′-H), 7.28–7.38 (m, 12 H, 3′-H, 6′-H, 2‴-H - 6‴-H, 2⁗-H - 6⁗-H), 7.44 (ddd, J = 7.5, 7.5, 1.3 Hz, 1 H, 5-H), 7.88 (dd, J = 7.6, 1.0 Hz, 1 H, 4-H), 10.3 (s, 1 H, 2-H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.4 (+, 2 C, C-7″, C-9″), 20.9 (+, C-8″), 52.6 (−, CH_2), 122.2 (+, C-6′), 122.8 (+, C-5′), 129.0 (+,4 C, C-3‴, C-5‴, C-3⁗, C-5⁗), 129.6 (+, C-5″), 130.0 (+, 2 C, C-4‴, C-4⁗), 130.2 (+, C-5), 130.5 ($C_{quat.}$, C-1″), 131.4 (+, C-4), 133.6 (+, 4 C, C-2‴, C-6‴, C-2⁗, C-6⁗), 134.1 ($C_{quat.}$, 2 C, C-2″, C-6″), 134.6 (+, C-4′), 137.1 (2 $C_{quat.}$, C-1‴, C-1⁗), 137.3 ($C_{quat.}$, C-2′), 138.1 (+, C-2), 139.6 ($C_{quat.}$, C-1′), 141.1 ($C_{quat.}$, C-4″).

$\mathbf{R}_f$ = 0.13 (SiO_2, DCM:MeOH = 8:1).

M.p. 221 °C (DCM/MeOH).

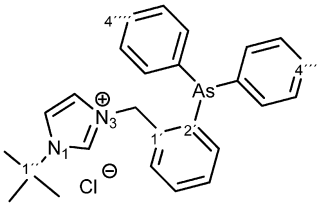
IR (KBr): ν = 3423, 3145, 3047, 1609, 1579, 1545, 1482, 1434, 1380, 1306, 1207, 1159, 1124, 1068, 1023, 999, 968, 935, 854, 823, 740, 697, 669, 634, 578, 473 cm^{-1}.

MS (ESI); m/z (%): 505 (100) $[M-Cl]^+$, 506 (34) $[M-Cl+H]^+$.

CHN: $C_{31}H_{30}AsClN_2$: cal. C 68.83, H 5.59, Cl 6.55, N 5.18. Found C 67.70, H 5.76, Cl 6.34, N 5.18%.

HRMS: $C_{31}H_{30}AsClN_2$: Cal. 540.1313;
$[M-Cl]^+$: Calc. 505.16195. Found 505.16188.

4.6. 1-tert-Butyl-3-(2-(diphenylarsinyl)benzyl)-1H-imidazol-3-ium chloride (*13*)



The procedure is the same as in **11** except for exchanging phenyl-imidazole (**8**) by 1-*tert*-butyl-imidazole (**10**) (2.58 mmol). The product was purified by chromatography (SiO_2; DCM:MeOH = 8:1) to give the *tert*-butyl-imidazolium chloride (980 mg, 82%).

^{1}H NMR (400 MHz, MeOD): δ = 1.47 (s, 9 H, 2″-H), 5.69 (s, 2 H, CH_2), 7.07 (dd, J = 1.2 Hz, 7.6 Hz, 1 H, 3′-H), 7.08–7.15 (m, 4 H, 3″-H, 5‴-H, 3⁗-H, 5⁗-H), 7.30–7.40 (m, 8 H, 5-H, 4′-H, 2‴-H, 6‴-H, 2⁗-H, 6⁗-H, 4‴-H, 4⁗-H), 7.52 (ddd, J = 7.5, 7.5, 1.3 Hz, 1 H, 5′-H), 7.61–7.63 (m, 2 H, 4-H, 6-′H), 9.10 (s, 1 H, 2-H).

^{13}C NMR (100 MHz, MeOD): δ = 29.6 (+, 3 C, C-2″), 54.1 (−, CH_2), 61.4 ($C_{quat.}$, C-1″), 121.6 (+, C-6′), 123.5 (+, C-4′), 130.17 (+, 4 C, C-2‴, C-6‴, C-2⁗, C-6⁗), 130.2 (+, 2 C, C-4‴, C-4⁗), 131.17 (+, C-5′), 131.2 (+, C-5), 132.4 (+, C-4), 133.9 (t, +, C-2), 134.6 (+, 4 C, C-3‴, C-5‴, C-3⁗, C-5⁗), 136.5 (+, C-3′), 138.8 ($C_{quat.}$, C-1′), 138.9 (2 $C_{quat.}$, C-1‴, C-1⁗), 141.4 ($C_{quat.}$, C-2′).

$\mathbf{R}_f$ = 0.32 (SiO_2, DCM:MeOH = 5:1).

M.p. 254–256 °C (DCM/MeOH).

IR (KBr): ν = 3385, 3158, 3116, 3065, 2991, 2937, 2876, 1960, 1880, 1622, 1578, 1552, 1479, 1446, 1431, 1376, 1305, 1240, 1209, 1155, 1136, 1119, 1073, 1024, 996, 973, 948, 910, 873, 818, 780, 752, 742, 693, 656, 632, 587, 474, 451, 413 cm^{-1}.

MS (ESI); m/z (%): 443 (100) $[M-Cl]^+$, 444 (23) $[M-Cl+H]^+$, 921 (8) $[M+M-Cl]^+$.

CHN: $C_{26}H_{28}AsClN_2$: Calc. C 65.21, H 5.89, Cl 7.40, N 5.85. Found C 64.63, H 5.99, Cl 7.50, N 6.19%.

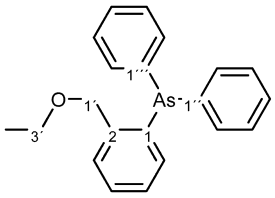
HRMS: $C_{26}H_{28}AsClN_2$: Calc. 478.1157;
$[M-Cl]^+$: Calc. 443.14630. Found 443.14644.

Table 8
Crystallographic data for compound **11**

Formula	$C_{28}H_{26}AsClN_2O$
Formula weight (g/mol)	516.88
Colour/habit	Colourless/block
Crystal size (mm)	0.32 × 0.29 × 0.25
Crystal system	Monoclinic
Space group	$P2_1/c$ (no. 14)
a (Å)	16.863(3)
b (Å)	9.411(1)
c (Å)	18.754(3)
α (°)	90
β (°)	123.07(1)
γ (°)	90
V (Å^3)	2494.1(7)
Z	4
T (K)	223(2)
μ (mm^{-1})	1.493
θ Range (°)	1.00–24.99
Index ranges (h, k, l)	±20; −10, +11; ±22
Measured reflections	22979
Independent reflections	4379
R_{int}	0.1165
Reflections with $[I > 2\sigma(I)]$	22160
Parameters	402
R_1 wR_2 $[I > 2\sigma(I)]$[a]	0.0664/0.0712
R_1 wR_2 (all data)[a]	0.0788/0.1138
GOF (on F^2)[a]	1020
Largest difference peaks and hole (e A^{-3})	+0.355 and −0.341

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$; $wR_2 = \{\Sigma\ [w(|F_o|^2-|F_c|^2)^2]/\Sigma\ [w(|F_o|^2)^2]\}^{1/2}$; GOF = $\{\Sigma\ [w(F_o^2-F_c^2)^2]/(n-p)\}^{1/2}$.

*4.7. (2-(Ethoxymethyl)phenyl)diphenylarsine (**14**)*



Milligram quantities of this ethylether were obtained as side product in the substitution reaction. The side product was purified by chromatography (SiO_2; PE:EE = 12:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.97 (t, J = 7.0 Hz, 3 H, 4′-H), 3.39 (q, J = 7.0 Hz, 2 H, 3′-H), 4.65 (s, 2 H, 1′-H), 6.99 (dd, J = 7.6, 1.0 Hz, 1 H, 6-H), 7.16 (ddd, J = 7.5, 7.5, 1.4 Hz, 1 H, 5-H), 7.26–7.34 (m, 11 H, 4-H, 2″-H, 6″-H, 2‴-H, 6‴-H), 7.42–7.76 (m, 1 H, 3-H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.8 (+, C-4′), 65.6 (−, C-3′), 72.2 (−, C-1′), 128.0 (+, C-5), 128.3 (+, C-3), 128.34 (+, C-4), 128.5 (+, 2 C, C-4″, C-4‴), 128.6 (+, 4 C, C-3″, C-5″, C-3‴, C-5‴), 133.8 (+, 4 C, C-2″, C-6″, C-2‴, C-6‴), 134.0 (+, C-6), 138.9 ($C_{quat.}$, C-1), 139.3 ($C_{quat.}$, C-1″, C-1‴), 142.6 ($C_{quat.}$, C-2).

R_f = 0.41 (SiO_2, PE:EE = 12:1).

M.p. 63–64 °C (PE:EE).

IR (KBr): ν = 3424, 3053, 2977, 2924, 2849, 1578, 1481, 1451, 1433, 1369, 1350, 1272, 1205, 1186, 1156, 1124, 1102, 1079, 1055, 1025, 998, 752, 741, 695, 474, 435 cm^{-1}.

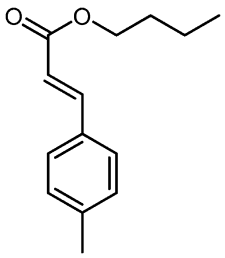
MS (DCP, 70 eV); m/z (%): 364 (100) [M^+], 335 (13) [$M^+-C_2H_5$], 287 (60) [$M^+-C_6H_5$], 257 (83), 241 (52), 166 (60), 152 (27) [$M^+-C_{15}H_{16}O$].

CHN: $C_{21}H_{16}AsO$: Calc. C 69.23, H 5.81. Found C 69.05, H 5.88%.

HRMS: $C_{21}H_{16}AsO$: Calc. 364.0808;
[M+Na]$^+$: Calc. 387.07006. Found 387.07001.

4.8. General procedure: Heck reaction

(*E*)-Butyl-3-*p*-tolyl acrylate (16) [25]

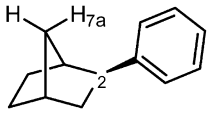


Under nitrogen atmosphere 5.6 mg (9.7 μmol) $Pd(dba)_2$ and (9.8 μmol) 1-substituted 1*H*-imidazolium salt (**11–13**) were dissolved in 2 mL dry DMAc. Then 490.6 mg (2.25 mmol) *p*-iodotoluene, 0.21 mL (1.5 mmol) butyl acrylate and 654 mg (2.0 mmol) cesium carbonate were added to the Schlenk-tube. The mixture was stirred at 60 °C for 20 h. Column chromatography (SiO_2, PE:EE = 30:1) gave the desired product in quantitative yield.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.96 (t, J = 7.2 Hz, 3 H, CH_3), 1.33–1.76 (m, 4 H, CH_2CH_2), 2.37 (s, 3 H, Ar-CH_3), 4.20 (t, J = 6.6 Hz, 2 H, OCH_2), 6.40 (d, J = 16.0 Hz, 1 H, C*H* = CH), 7.19 (d, J = 8.1 Hz, 2 H, $H_{arom.}$), 7.43 (d, J = 8.2 Hz, 2 H, $H_{arom.}$), 7.66 (d, J = 15.8 Hz, 1 H, CH = C*H*).

4.9. General procedure: hydro-Heck reaction

2-*exo*-Phenylnorbornane (**18**) [12e]

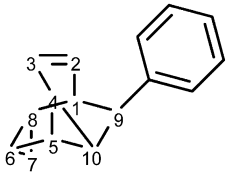


Under nitrogen atmosphere 28.8 mg (50 μmol) $Pd(dba)_2$ and (220 μmol) 1-substituted 1*H*-imidazolium salt (**11–12**) were dissolved in 3 mL dry DMSO. After stirring for 15 min at 60 °C 612 mg (3 mmol) iodobenzene, 188 mg (2 mmol) norbornene, 976 μL (7 mmol) dry Et_3N and 226 μL (6 mmol) formic acid were added to the Schlenk-tube. The mixture was stirred at 60 °C for 22 h. Column chromatography (SiO_2, PE) gave the desired product in 81–86% yield.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.13–1.23 (m, 1 H, 7-H_b), 1.24–1.37 (m, 2 H, 5-H_{endo}, 6-H_{endo}), 1.44–1.83 (m, 5 H, 7-H_a, 5-H_{exo}, 6-H_{exo}, 3-$H_{exo,}$ 3-H_{endo}), 2.30–2.40 (m, 2 H, 1-H, 4-H), 2.74 (dd, J = 8.0, 6.3 Hz, 1 H, 2-H_{endo}), 7.08–7.34 (m, 5 H, $H_{arom.}$).

4.10. General procedure: Π, σ Domino-Heck reaction

9-Phenyltetracyclo[3.3.2.0^{6,8}.0^{4,10}]dec-2-ene (**20**) [12a]

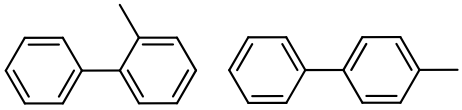


Under nitrogen atmosphere 5.6 mg (25 μmol) $Pd(OAc)_2$ and (110 μmol) 1-substituted 1*H*-imidazolium salt (**11–12**) were dissolved in 3 mL dry DMF. After stirring for 15 min at 60 °C 306 mg (1.5 mmol) iodobenzene, 132 mg (1 mmol) bishomobarrelene (**19**), 558 μL (4 mmol) dry Et_3N and 113 μL (3 mmol) formic acid were added to the Schlenk-tube. The mixture was stirred at 60 °C for 19 h. Then 5 mL water and 10 mL pentane was added. The aqueous layer was extracted three times with each 5 mL pentane. The combined organic phases were dried over $MgSO_4$, filtered and evaporated to dryness. Column chromatography (SiO_2, PE) gave the desired product in 42–48% yield.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.13–0.30 (m, 1 H, 7-H), 0.47 (dd, J = 9.0, 5.2 Hz, 1 H, 7-H), 0.94–1.08 (m, 1 H, 6-H), 1.09–1.24 (m, 1 H, 8-H), 1.36–1.50 (m, 1 H, 10-H), 1.57–1.79 (m, 2 H, 5-H, 4-H), 2.62–2.74 (m, 1 H, 1-H), 3.22 (bs, 1 H, 9-H), 5.68 (dd, J = 9.3, 6.5 Hz, 1 H, 2-$H_{olefin.}$), 6.05 (dd, J = 9.3, 5.8 Hz, 1 H, 3-$H_{olefin.}$), 7.08–7.27 (m, 5 H, $H_{arom.}$).

4.11. General procedure: Suzuki reaction

2-Methylbiphenyl (**22a**), 4-methylbiphenyl (**22b**)[26]



22a **22b**

Under nitrogen atmosphere 1.1 mg (5 μmol) $Pd(OAc)_2$, (5 μmol) 1-substituted 1*H*-imidazolium salt (**11–12**) and 651.6 mg (2 mmol) cesium carbonate were suspended in 3 mL dry DMAc. After stirring for 5 min at 60 °C 218 mg (1 mmol) iodotoluene, 182.9 mg (1.5 mmol) phenylboronic acid (**21**) was added to the Schlenk-tube. The mixture was stirred at 60 °C for 19 h. Column chromatography (SiO_2, PE) gave the desired methylbiphenyl in 87–99% yield.

22a: ^{1}**H NMR** (400 MHz, $CDCl_3$): δ = 2.27 (s, 3 H, CH_3), 7.22–7.29 (m, 4 H, $H_{arom.}$), 7.30–7.37 (m, 3 H, $H_{arom.}$), 7.38–7.43 (m, 2 H, $H_{arom.}$).

22b: ^{1}**H NMR** (400 MHz, $CDCl_3$): δ = 2.36 (s, 3 H, CH_3), 7.18–7.25 (m, 2 H, $H_{arom.}$), 7.26–7.33 (m, 1 H, $H_{arom.}$), 7.36–7.43 (m, 2 H, $H_{arom.}$), 7.45–7.50 (m, 2 H, $H_{arom.}$), 7.53–7.59 (m, 2 H, $H_{arom.}$).

6. Supplementary material

CCDC 678532 (3a) and 675658 (11) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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