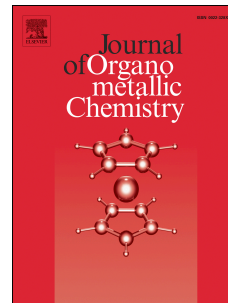


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Preparation and catalytic properties of the triphenylarsine and triphenylstibine-stabilized tri-heteroleptic NHC—Pd—allyl complexes

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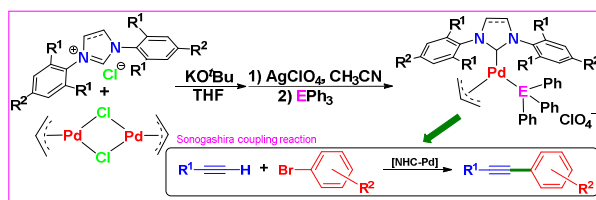
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Graphical abstract



The graphical abstract synopsis:

A series of triphenylarsine and triphenylstibine-stabilized tri-heteroleptic NHC-Pd-allyl complexes were synthesized and used in Sonogashira coupling reaction.

Highlights

- Triphenylarsine and triphenylstibine-stabilized tri-heteroleptic NHC-Pd-allyl complexes were synthesized.
- Molecular structures have been elucidated by X-ray single-crystal diffraction.
- The catalytic activities of the complexes were examined in Sonogashira coupling reaction.

Preparation and catalytic properties of the triphenylarsine and triphenylstibine-stabilized tri-heteroleptic NHC–Pd–allyl complexes

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Abstract

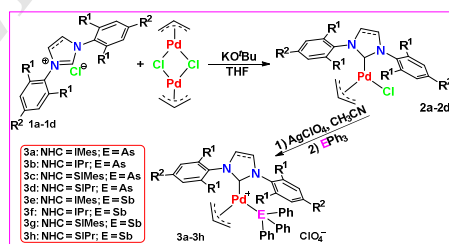
A series of triphenylarsine and triphenylstibine-stabilized tri-heteroleptic NHC–Pd–allyl complexes were synthesized and characterized. The solid-state structures of the complexes shown mononuclear carbene palladium complexes, in which, each palladium centre was coordinated by an *N*-heterocyclic carbene, the η^3 -coordinated allyl moiety and an As or Sb donor. Further investigation of the Pd complexes as catalysts in Sonogashira coupling reaction was carried out and the obtained complexes exhibited good reactivities for aryl bromides.

Keywords: *N*-Heterocyclic carbene, Palladium complexes, Triphenylarsine, Triphenylstibine, Sonogashira coupling reaction.

1. Introduction

The chemical property of the transition metal complexes is significantly influenced by the coordination of the ligand in transferring electronic density to the metal centre.^[1] Recently years, the predominant performances of the *N*-heterocyclic carbene (NHC) palladium catalysts in cross-coupling reactions have aroused great interest.^[2] A number of well-defined NHC–Pd(II) complexes have been widely exploited in organic synthesis. Further study shown that the activity of the NHC–Pd(II) complexes can be modified by the introduction of the ancillary ligands. For example, Nolan's NHC-palladacycles, allyl-based NHC–Pd(II) complexes, acac-based NHC–Pd(II) complexes and Organ's Pd-PEPPSI-NHC complexes have exhibited good catalytic

activities due to the weak coordinating ancillary ligands can disassociate from the metal centre to form catalytically active species with vacant coordination sites and then re-coordinate to it after the catalytic cycle.^[3] In order to further explore the catalytic activities of NHC–Pd(II) complexes, some heteroatomic compound have been introduced into the coordination with the palladium centres and these complexes bearing mixed ligands may have potential application in organic synthesis. Among the known dual-ligand systems, the combination of NHC with phosphine is of special interest, due to the important role of phosphines in catalysis as well as the synergistic effect of these two ligands.^[4] Recently, the phosphino-carbene–Pd(II)–allyl complexes have been investigated in detail in order to determine the influence of the *trans* effect of the complexes.^[5] Despite the progress made so far in the use of mixed-ligand complexes to promote catalysis, very little research has been reported on heteroleptic NHC–Pd complexes with group 15 donor ligands. Recently, we have reported the synthesis and application of triphenylarsine and triphenylstibine-stabilized NHC–Pd complexes (NHC)PdCl₂(EPh₃) (E = As, Sb).^[6] With one of our efforts being the development of well-defined NHC–Pd complexes and their utility in catalysis, herein we reported the synthesis and characterization of triphenylarsine and triphenylstibine-stabilized tri-heteroleptic NHC–Pd–allyl complexes [(NHC)Pd(allyl)(EPh₃)]ClO₄ (E = As, Sb) (**3a–3h**) and their further utility in Sonogashira coupling reaction.



Scheme 1. Synthesis of the well-defined tri-heteroleptic NHC–Pd–allyl complexes [(NHC)Pd(allyl)(EPh₃)]ClO₄ (E = As, Sb) (**3a–3h**)

2. Results and Discussion

2.1 Synthesis of the [(NHC)Pd(allyl)(EPh₃)]ClO₄ (E = As, Sb) complexes

The [(NHC)Pd(allyl)(EPh₃)]ClO₄ complexes were prepared in one pot based on anion metathesis and then ligand replacement with EPh₃ (NHC: IMes = *N,N'*-bis-

(2,4,6-trimethylphenyl)imidazol-2-ylidene; IPr = *N,N'*-bis-(2,6-di(isopropyl)phenyl)imidazol-2-ylidene; SIMes = *N,N'*-bis-(2,4,6-trimethylphenyl)imidazolidin-2-ylidene; SIPr = *N,N'*-bis-(2,6-di(isopropyl)phenyl)imidazolidin-2-ylidene; E = As, Sb). As shown in Scheme 1, following the synthetic route reported previously, the (NHC)Pd(allyl)Cl complexes were easily obtained from reaction of imidazolium salts, [Pd(allyl)Cl]₂ and KO^tBu in dry THF.^[7] The anion metathesis of (NHC)Pd(allyl)Cl with AgClO₄ in CH₃CN generated the solvated complexes [(NHC)Pd(allyl)(CH₃CN)]ClO₄ (**2a–2d**) in almost quantitative yields. The obtained complexes subsequently reacted with EPh₃ through ligand replacement to afford the above-mentioned products (**3a–3h**). Complexes **3a–3h** have been fully characterized by ¹H NMR, ¹³C NMR, elemental analysis, HR-MS and X-ray single-crystal diffraction. The formation of the heteroleptic complexes is evident from the characteristic proton signal resonances of NHC, allyl moiety (one heptet and four doublets) and EPh₃ in ¹H NMR spectra. Furthermore, the ¹³C NMR spectra revealed the appearance of the carbonyl carbons as diagnostic singlet peaks (156.3–156.1 ppm for IMes and IPr-bearing complexes; 187.1–186.5 ppm for SIMes and SIPr-bearing complexes). All of the complexes were further characterized by X-ray single-crystal diffraction and the structures were depicted in Figure 1. In all cases the common distorted square-planar coordination around the palladium center with an environment of an NHC, the allyl moiety and an As or Sb donor was observed. The allyl moiety is η³-coordinated to the palladium with one terminal carbon *trans* to the carbene and the second terminal carbon *trans* to EPh₃. Among the eight complexes, the Pd–C_{NHC} bond lengths were in a range of 2.041(7)–2.087(8) Å with the shortest distance is found for **3a** and the longest for **3d**, which suggested a single bond of σ-bond character. The Pd–C_{allyl} bond lengths were in a range of 2.124(10)–2.192(10) Å with the shortest distance is found for **3e** and the longest for **3d**. In all complexes, the Pd–C_{NHC} bond lengths were slightly longer than that of the Pd–C_{allyl} bonds. In addition, the Pd–As(Sb) bond lengths, which were in narrow ranges [2.4338(12)–2.4506(13) Å for Pd–As bonds and 2.572(2)–2.5888(12) Å for Pd–Sb bonds], were significantly longer than the Pd–C bonds.

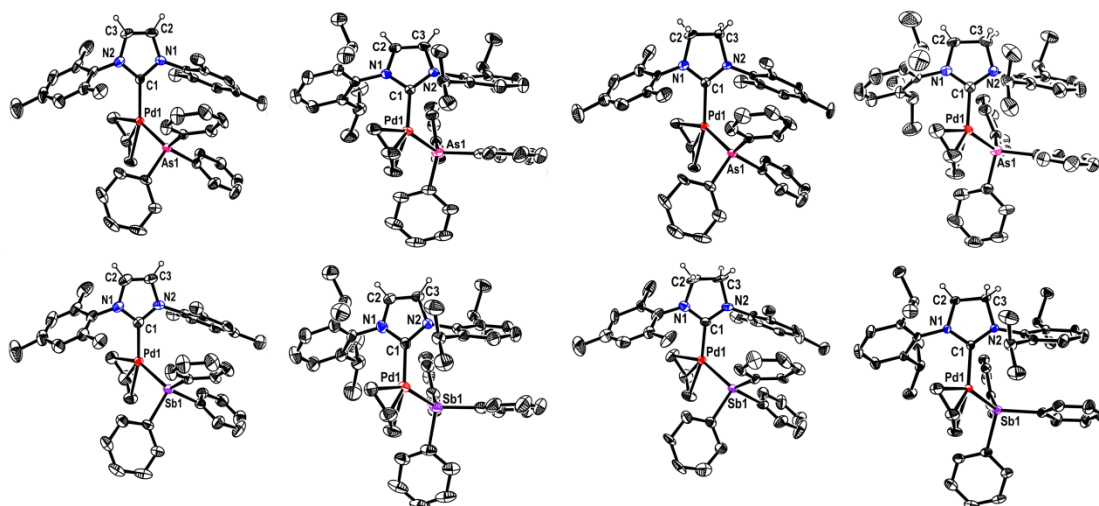


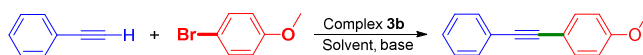
Figure 1. ORTEP diagrams of complexes **3a–3h** with thermal displacement parameters drawn at 30% probability. The anions (ClO_4^-), solvent molecules (CH_2Cl_2 or CHCl_3) and parts of the hydrogen atoms have been omitted for clarity.

2.2 The catalytic activities of complexes **3a–3h** for Sonogashira coupling reaction

The traditional palladium-catalyzed Sonogashira reaction often requires an amount of copper salt as co-catalyst, which led to the formation of air-sensitive copper acetylide species. However, the copper acetylides often participate in the Glaser-Hay homo-coupling, which reduced the yields of the Sonogashira reaction.^[8] In this connection, the Sonogashira reaction performed under Cu-free conditions resulted in a significant improvement in the performance of these reactions. In recently years, modified protocols have mainly focused on the development of new Pd-catalysts for the reaction and a number of examples of Sonogashira reaction catalyzed by NHC–Pd catalysts have been reported.^[9] In order to demonstrate the utility of these tri-heteroleptic Pd-complexes, complexes **3a–3h** were subjected to the Cu-free Sonogashira reaction of phenylacetylene with aryl bromides. Initially, complex **3b** (1.0 mol%) was selected as the model catalyst, the reaction of 4-bromoanisole (0.5 mmol) with phenylacetylene (0.6 mmol) as a model reaction to test the reaction conditions and in particular the solvent and base. As shown in Table 1, using DMF as solvent and Cs_2CO_3 as base gave the best yield at 100 °C in 6 h (Table 1, entry 1). Under the same conditions, using K_2CO_3 as the base could also give a similar result.

However, other inorganic bases, like Na_2CO_3 , KHCO_3 , KOH and KO^tBu have been tested to lead to relatively poor yields. The solvent was then investigated and the role of the solvent appeared to be crucial in the reaction with complex **3b** as catalyst. With regard to reaction solvent, DMF is found to be a superior solvent for this process. Moreover, products can also be obtained in high yields when DMA was used as solvent. A plausible reason is that the catalytically active Pd(0) species could be generated readily from the precatalysts $[(\text{NHC})\text{Pd}(\text{allyl})(\text{EPh}_3)]\text{ClO}_4$ and remain stable in DMF or DMA. However, in the presence of other solvents such as DMSO, moderate yield was obtained. When 1,4-dioxane, CH_3CN and THF were used, no reaction occurred. The catalyst loading and reaction temperature were then tested. When the catalyst loading was reduced to 0.5 mol%, the yield lowered to 65% (Entry 12). However, the yields could be increased slightly when the time was prolonged (Entry 13). Furthermore, the reaction temperature was also investigated and the optimum reaction temperature was found to be 100 °C. With the increase of temperature, the catalytic activity of complex **3b** decreased gradually which indicated that the catalysts suitable for the coupling reaction but tend to decompose at higher temperatures. Moreover, the model reaction was performed in the presence of a nitrogen atmosphere, complex **3b** showed a similar performance of the reaction as that in air atmosphere (Entry 16). However, an oxygen atmosphere could result into lower yield of the product (Entry 17), which probably indicated that the oxidative decomposition of the catalyst in the presence of oxygen. On the basis of the extensive screening, DMF and Cs_2CO_3 were proved to be the efficient solvent and base, respectively, with 1.0 mol % complex **3b** at 100 °C for 6 h, thus giving the optimal coupling result. Under the same conditions, other complexes were also tested, the (S)IPr-based complexes **3b**, **3d**, **3f** and **3h** with the sterically bulky substituent groups gave high yields, however, the (S)IMes-based complexes **3a**, **3c**, **3e** and **3g** gave very low yields in both cases.

Table 1. Study of the reaction conditions for complex **3b** catalyzed Sonogashira reaction of 4-bromoanisole with phenylacetylene^a



Entry	[Pd] [%]	Solvent	Base	Yield ^b (%)
1	3b (1.0%)	DMF	Cs ₂ CO ₃	91
2	3b (1.0%)	DMF	K ₂ CO ₃	87
3	3b (1.0%)	DMF	Na ₂ CO ₃	64
4	3b (1.0%)	DMF	KHCO ₃	52
5	3b (1.0%)	DMF	KOH	40
6	3b (1.0%)	DMF	KO ^t Bu	45
7	3b (1.0%)	DMA	Cs ₂ CO ₃	88
8	3b (1.0%)	DMSO	Cs ₂ CO ₃	65
9	3b (1.0%)	1,4-dioxane	Cs ₂ CO ₃	20
10	3b (1.0%)	CH ₃ CN	Cs ₂ CO ₃	trace
11	3b (1.0%)	THF	Cs ₂ CO ₃	trace
12	3b (0.5%)	DMF	Cs ₂ CO ₃	65
13 ^c	3b (0.5%)	DMF	Cs ₂ CO ₃	72
14 ^d	3b (1.0%)	DMF	Cs ₂ CO ₃	80
15 ^e	3b (1.0%)	DMF	Cs ₂ CO ₃	72
16 ^f	3b (1.0%)	DMF	Cs ₂ CO ₃	92
17 ^g	3b (1.0%)	DMF	Cs ₂ CO ₃	54
18	3a (1.0%)	DMF	Cs ₂ CO ₃	50
19	3c (1.0%)	DMF	Cs ₂ CO ₃	42
20	3d (1.0%)	DMF	Cs ₂ CO ₃	90
21	3e (1.0%)	DMF	Cs ₂ CO ₃	40
22	3f (1.0%)	DMF	Cs ₂ CO ₃	88
23	3g (1.0%)	DMF	Cs ₂ CO ₃	35
24	3h (1.0%)	DMF	Cs ₂ CO ₃	85

^a Reaction conditions: 4-bromoanisole (0.5 mmol), phenylacetylene (0.6 mmol), complex **3b** (0.005 mmol), base (0.6 mmol), solvent (2.0 mL), 100 °C, 6 h. ^b Isolated yield. ^c Reaction time is 12h. ^d Reaction temperature is 130 °C. ^e Reaction temperature is 80 °C. ^f Under nitrogen atmosphere. ^g Under oxygen atmosphere.

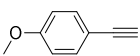

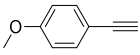
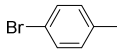
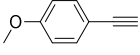
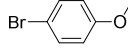
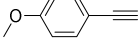
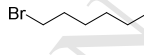
The coupling reactions of a wide range of aryl bromides with terminal alkynes were further studied in the presence of complexes **3b**, **3d**, **3f** and **3h**, the results for this reaction are reported in Table 2. Usually, electron-withdrawing groups have an effect on increasing the reactivity of substrates. In this case, gratifyingly, all complexes were found to be able to efficiently convert activated aryl bromides in 6 h. The couplings of activated aryl bromide (such as 4-bromoacetophenone and 4-bromonitrobenzene) with phenylacetylene afforded excellent yields (Table 2, entries 1–8). Thus, to investigate the effects of the catalytic system with an electron-donating substrate and neutral aryl bromide, we performed the reaction between phenylacetylene with 4-bromotoluene and bromobenzene under similar reaction condition, respectively. The corresponding products were obtained in moderate yields when 4-bromotoluene or bromobenzene was used (Entries 9–16), which are inferior to the reactions of activated aryl bromides. The system also proved to be tolerant of sterically hindered substrates, while with an *ortho* or *meta*-substituted aryl bromide, a relatively lower yield was isolated under the present reaction conditions owing to steric hindrance put by substituents. Furthermore, the coupling reactions of substituted aryl acetylenes with aryl and alkyl bromides were also attempted. For example, the couplings of 4-methoxyphenylacetylene with aryl bromides (such as 4-bromotoluene and 4-bromoanisole) afforded good to excellent yields (Entries 25–32). Moreover, the couplings of 4-methoxyphenylacetylene with 1-bromohexane also gave relatively good yields (Entries 33–36). However, this catalytic system was no longer effective for aryl chlorides. No desired Sonogashira coupling product was obtained for the reaction of aryl chloride with phenylacetylene.

As can be seen from the results above, the reactivities of the obtained complexes are not limited to *para*-substituted aryl bromides, *ortho*- or *meta*-substituted aryl bromides and alkyl bromides can be also employed. Yields are somewhat lower compared with *para*-substituted aryl bromides, and are found to significantly depend on the steric hindrance of the substituent. Furthermore, the electronic properties of the substituent of aryl bromides also influence the reaction yield to some extent. On the other hand, the reaction fails when aryl chlorides are employed as substrates.

Consequently, the substrate scope of these obtained Pd-catalysts appears somewhat lower activities in comparison with some recently reported Pd-catalysts. With the results in hand and in every case studied, the catalysts **3b** and **3d** (with As donor) are slightly more active than the catalysts **3f** and **3h** (with Sb donor). We attributed these performance differences to the well-balanced property between NHC and As donor in the catalytic cycle. As the ancillary ligand, it is known that despite the Sb-donor can form very similar complexes with P and As-donors, the stibine owned the poorer donor properties compared to arsine ligand as well as an increased tendency to dissociation in solution in contrast with their arsine homologues.^[10] Furthermore, the (S)IPr-based complexes with the sterically bulky substituent groups shown more efficient catalytic activities than the (S)IMes-based complexes. This suggests that the well-balanced property between NHC and As (Sb) donor do not influence the reaction yield to a great extent, whereas the steric effects of the NHC ligands are more important.

Table 2 Sonogashira coupling reaction of aryl bromides with alkynes^{a,b}

Entry	Catalyst	Alkynes	Aryl bromides	Yield (%) ^b
1	3b			94
2	3d			92
3	3f			88
4	3g			88
5	3b			96
6	3d			94
7	3f			91
8	3g			90
9	3b			84
10	3d			87
11	3f			82
12	3g			80
13	3b			80
14	3d			82
15	3f			77
16	3g			75
17	3b			86

18	3d		84
19	3f		80
20	3g		80
21	3b		74
22	3d		72
23	3f		65
24	3g		62
25	3b		90
26	3d		90
27	3f		85
28	3g		85
29	3b		96
30	3d		95
31	3f		92
32	3g		90
33	3b		85
34	3d		82
35	3f		78
36	3g		80

^a Reaction conditions: aryl bromide (0.5 mmol), terminal alkyne (0.6 mmol), NHC–Pd (0.005 mmol), Cs₂CO₃ (0.6 mmol), DMF (2.0 mL) at 100 °C for 6 h. ^b Isolated yield.

3. Conclusions

In summary, a series of triphenylarsine and triphenylstibine-stabilized tri-heteroleptic NHC–Pd–allyl complexes were synthesized and fully characterized. Analyses of crystal structures show that each palladium centre was coordinated by an *N*-heterocyclic carbene, the allyl moiety and an As or Sb donor. The investigation of catalytic activities of the obtained complexes shown that the (S)IPr-based complexes with the sterically bulky substituent groups can effectively catalyze the Sonogashira coupling reaction of aryl bromide with terminal alkynes. Further studies on the well-defined NHC–Pd complexes, as well as their applications in organic synthesis is currently undergoing in our laboratory.

4. Experimental section

4.1 General considerations

The chemicals were purchased from commercial suppliers and were used without purification prior to use unless otherwise indicated. NMR spectra were recorded at

400 MHz (for ^1H NMR) and 100 MHz (for ^{13}C NMR) on a Bruker Avance 400 NMR spectrometer. All ^1H , and ^{13}C NMR were performed in CDCl_3 with tetramethylsilane (TMS) as an internal standard. The C, H, and N analyses were performed with a Vario El III elemental. Complexes (NHC)Pd(allyl)Cl (**2a–2d**) were prepared according to the literature.^[11]

4.2 Synthesis of complexes 3a–3h

A round-bottom flask equipped with a stir bar was charged with the (NHC)Pd(allyl)Cl (0.5 mmol), AgClO_4 (0.55 mmol, 104 mg) and CH_3CN (5.0 mL). The reaction mixture was stirred at room temperature for 1 h and a solution of AsPh_3 or SbPh_3 (0.5 mmol) in CH_2Cl_2 (5.0 mL) was added dropwise with stirring. The reaction mixture was stirred for a further 4 h. The solvents were removed under reduced pressure and the residue was purified by flash chromatography on short silica gel and recrystallized from *n*-hexane– CH_2Cl_2 to afford the desired products. Single crystals of the complexes for X-ray diffraction analysis were obtained from evaporation of their *n*-hexane/ CH_2Cl_2 or CHCl_3 solutions.

[(IMes)Pd(Allyl)(AsPh₃)]ClO₄ (**3a**)

The procedure yielded 385 mg (90%) of the pure **3a** as a white powder. ^1H NMR (CDCl_3 , 400 MHz) δ (ppm) = 7.43 (t, J = 7.2 Hz, 3H, *p*-CH-phenyl), 7.34 (s, 2H, *m*-CH-aniline), 7.32 (t, J = 7.2 Hz, 6H, *m*-CH-phenyl), 6.96 (br, 4H, N-CH=CH-N and *m*-CH-aniline), 6.90 (d, J = 6.8 Hz, 6H, *o*-CH-phenyl), 5.08 (sept, J = 6.8 Hz, 1H, CH-allyl), 4.22 (dd, J = 6.8 and 1.6 Hz, 1H, CH_2 -allyl), 3.35 (dd, J = 7.2 and 1.6 Hz, 1H, CH_2 -allyl), 2.47 (d, J = 13.2, 1H, CH_2 -allyl), 2.33 (s, 6H, *p*- CH_3 -aniline), 2.29 (d, J = 13.6 Hz, 1H, CH_2 -allyl), 1.99 (s, 12H, *o*- CH_3 -aniline). ^{13}C NMR (CDCl_3 , 100 MHz): δ (ppm) = 178.39 (C_{carbene}), 139.48 (C_{aniline}), 134.47 (C_{phenyl}), 132.65 (*o*- C_{phenyl}), 130.46 (C_{aniline}), 129.45 (*p*- C_{phenyl}), 129.15 (*m*- C_{phenyl}), 125.09 (N-CH=CH-N), 119.01 (C_{aniline}), 71.04 (CH-allyl), 67.59 (CH_2 -allyl), 20.89 (*p*- CH_3 -aniline), 18.36 (*o*- CH_3 -aniline), 18.02 (*o*- CH_3 -aniline). HR-MS (ESI): calcd for $\text{C}_{42}\text{H}_{44}\text{AsN}_2\text{Pd}$ [$\text{M} - \text{ClO}_4$] $^+$ 757.1755; found 757.1784. Calcd. for [(IMes)Pd(Allyl)(AsPh₃)]ClO₄ ($\text{C}_{42}\text{H}_{44}\text{AsClN}_2\text{O}_4\text{Pd}$): C, 58.82; H, 5.17; N, 3.27%. Found: C, 58.55; H, 5.33; N, 3.56%.

[(IPr)Pd(Allyl)(AsPh₃)]ClO₄ (3b)

The procedure yielded 410 mg (87%) of the pure **3b** as a white powder. ¹H NMR (CDCl₃, 400 MHz) δ (ppm): 7.61 (s, 2H, N-CH=CH-N), 7.41 (t, $J = 7.0$ Hz, 3H, *p*-CH-phenyl), 7.29 (t, $J = 7.5$ Hz, 6H, *m*-CH-phenyl), 7.27–7.26 (m, 2H, *p*-CH-aniline), 7.18 (br, 3H, *m*-CH-aniline), 6.93 (d, $J = 6.0$ Hz, 6H, *m*-CH-phenyl), 6.73 (br, 1H, *m*-CH-aniline), 5.13 (sept, $J = 6.5$ Hz, 1H, CH-allyl), 4.27 (d, $J = 7.0$ Hz, 1H, CH₂-allyl), 3.29 (d, $J = 7.5$ Hz, 1H, CH₂-allyl), 2.96 (br, 2H, CH(CH₃)₂), 2.52 (br, 2H, CH(CH₃)₂), 2.29 (d, $J = 13.5$ Hz, 1H, CH₂-allyl), 2.09 (d, $J = 13.0$ Hz, 1H, CH₂-allyl), 1.32 (br, 6H, CH(CH₃)₂), 1.15 (br, 6H, CH(CH₃)₂), 1.02 (br, 6H, CH(CH₃)₂), 0.70 (br, 3H, CH(CH₃)₂), 0.24 (br, 3H, CH(CH₃)₂). ¹³C NMR (CDCl₃, 100 MHz) δ (ppm): 181.54 (C_{carbene}), 145.14 (C_{aniline}), 133.56 (C_{phenyl}), 133.52 (*o*-C_{aniline}), 132.51 (C_{aniline}), 131.01 (*p*-C_{phenyl}), 130.55 (C_{aniline}), 129.35 (*m*-C_{phenyl}), 127.01 (N-CH=CH-N), 119.19 (C_{aniline}), 73.11 (CH-allyl), 67.95 (CH₂-allyl), 28.72 (CH(CH₃)₂), 28.50 (CH(CH₃)₂), 26.96 (CH(CH₃)₂), 25.73 (CH(CH₃)₂), 22.60 (CH(CH₃)₂), 22.52 (CH(CH₃)₂). HR-MS (ESI): calcd for C₄₈H₅₆AsN₂Pd [M – ClO₄]⁺ 841.2694; found 841.2687. Calcd. for [(IPr)Pd(Allyl)(AsPh₃)]ClO₄ (C₄₈H₅₆AsClN₂O₄Pd): C, 61.22; H, 5.99; N, 2.97%. Found: C, 60.96; H, 5.73; N, 3.18%.

[(SIMes)Pd(Allyl)(AsPh₃)]ClO₄ (3c)

The procedure yielded 390 mg (91%) of the pure **3c** as a white powder. ¹H NMR (CDCl₃, 400 MHz) δ (ppm): 7.42 (t, $J = 7.2$ Hz, 3H, *p*-CH-phenyl), 7.32 (t, $J = 7.6$ Hz, 6H, *m*-CH-phenyl), 7.00 (s, 1H, *m*-CH-aniline), 6.96 (s, 1H, *m*-CH-aniline), 6.89 (d, $J = 7.6$ Hz, 6H, *o*-CH-phenyl), 6.80 (s, 1H, *m*-CH-aniline), 6.51 (s, 1H, *m*-CH-aniline), 4.93 (sept, $J = 6.8$ Hz, 1H, CH-allyl), 4.33 (d, $J = 6.4$ Hz, 1H, CH₂-allyl), 4.15 (s, 4H, N-CH₂-CH₂-N), 3.19 (d, $J = 7.2$ Hz, 1H, CH₂-allyl), 2.42 (s, 3H, *o*-CH₃-aniline), 2.40 (d, $J = 13.2$, 1H, CH₂-allyl), 2.31 (s, 6H, *p*-CH₃-aniline), 2.23 (s, 3H, *o*-CH₃-aniline), 2.16 (d, $J = 13.2$ Hz, 1H, CH₂-allyl), 2.02 (s, 3H, *o*-CH₃-aniline), 1.64 (s, 3H, *o*-CH₃-aniline). ¹³C NMR (CDCl₃, 100 MHz) δ (ppm): 208.13 (C_{carbene}), 138.62 (C_{aniline}), 138.34 (C_{aniline}), 135.56 (C_{phenyl}), 135.02 (C_{aniline}), 134.55 (C_{aniline}), 132.72 (*o*-C_{phenyl}), 130.43 (C_{aniline}), 129.43 (*p*-C_{phenyl}), 129.11 (*m*-C_{phenyl}), 118.86 (C_{aniline}),

71.70 (CH-allyl), 67.33 (CH₂-allyl), 52.17 (N-CH₂-CH₂-N), 51.99 (N-CH₂-CH₂-N), 20.92 (*p*-CH₃-aniline), 18.69 (*o*-CH₃-aniline), 18.19 (*o*-CH₃-aniline), 18.09 (*o*-CH₃-aniline), 17.84 (*o*-CH₃-aniline). HR-MS (ESI): calcd for C₄₂H₄₆AsN₂Pd [M – ClO₄]⁺ 759.1912; found 759.1923. Calcd. for [(SImes)Pd(Allyl)(AsPh₃)]ClO₄ (C₄₂H₄₆AsClN₂O₄Pd): C, 58.68; H, 5.39; N, 3.26%. Found: C, 58.94; H, 5.21; N, 3.49%.

[(SIPr)Pd(Allyl)(AsPh₃)]ClO₄ (3d)

The procedure yielded 420 mg (89%) of the pure **3d** as a white powder. ¹H NMR (CDCl₃, 400 MHz) δ (ppm): 7.42 (t, *J* = 7.0 Hz, 3H, *p*-CH-phenyl), 7.34 (br, 6H, *m*-CH-phenyl), 7.28 (t, *J* = 7.0 Hz, 2H, *p*-CH-aniline), 7.19–7.17 (m, 2H, *m*-CH-aniline), 7.12 (t, *J* = 7.5 Hz, 2H, *o*-CH-phenyl), 7.12 (br, 3H, *o*-CH-phenyl), 7.01–7.00 (br, 2H, *m*-CH-aniline), 6.61 (d, *J* = 7.5 Hz, 1H, *o*-CH-phenyl), 5.01 (sept, *J* = 6.5 Hz, 1H, CH-allyl), 4.68 (q, *J* = 11.0 Hz, 1H, N-CH₂-CH₂-N), 4.59 (td, *J* = 11.0 and 5.5 Hz, 1H, N-CH₂-CH₂-N), 4.26 (td, *J* = 11.0 and 5.5 Hz, 1H, N-CH₂-CH₂-N), 4.09 (q, *J* = 11.0 Hz, 1H, N-CH₂-CH₂-N), 4.01 (d, *J* = 7.0 Hz, 1H, CH₂-allyl), 3.51 (sept, *J* = 6.5 Hz, 1H, CH(CH₃)₂), 3.34 (sept, *J* = 6.5 Hz, 2H, CH(CH₃)₂), 3.22 (sept, *J* = 6.5 Hz, 1H, CH(CH₃)₂), 3.18 (d, *J* = 7.0 Hz, 1H, CH₂-allyl), 2.23 (d, *J* = 13.5 Hz, 1H, CH₂-allyl), 1.86 (d, *J* = 13.0 Hz, 1H, CH₂-allyl), 1.49 (d, *J* = 6.5 Hz, 3H, CH(CH₃)₂), 1.36 (d, *J* = 6.5 Hz, 3H, CH(CH₃)₂), 1.34 (d, *J* = 7.0 Hz, 3H, CH(CH₃)₂), 1.24 (d, *J* = 7.0 Hz, 3H, CH(CH₃)₂), 1.11 (d, *J* = 6.5 Hz, 3H, CH(CH₃)₂), 1.07 (d, *J* = 6.5 Hz, 3H, CH(CH₃)₂), 0.71 (d, *J* = 6.5 Hz, 3H, CH(CH₃)₂), 0.19 (d, *J* = 6.5 Hz, 3H, CH(CH₃)₂). ¹³C NMR (CDCl₃, 100 MHz) δ (ppm): 210.37 (C_{carbene}), 146.92 (C_{aniline}), 146.74 (C_{aniline}), 146.18 (C_{aniline}), 145.78 (C_{aniline}), 136.55 (C_{phenyl}), 135.54 (C_{aniline}), 132.64 (C_{aniline}), 130.51 (*o*-C_{phenyl}), 130.06 (C_{aniline}), 129.84 (*p*-C_{phenyl}), 129.34 (*m*-C_{phenyl}), 125.02 (C_{aniline}), 124.67 (C_{aniline}), 124.55 (C_{aniline}), 124.04 (C_{aniline}), 119.21 (C_{aniline}), 73.83 (CH-allyl), 67.37 (CH₂-allyl), 55.63 (N-CH₂-CH₂-N), 55.19 (N-CH₂-CH₂-N), 28.97 (CH(CH₃)₂), 28.62 (CH(CH₃)₂), 28.50 (CH(CH₃)₂), 28.30 (CH(CH₃)₂), 27.09 (CH(CH₃)₂), 27.03 (CH(CH₃)₂), 26.94 (CH(CH₃)₂), 26.23 (CH(CH₃)₂), 23.84 (CH(CH₃)₂), 23.75 (CH(CH₃)₂), 23.35 (CH(CH₃)₂), 22.54 (CH(CH₃)₂). HR-MS (ESI): calcd for C₄₂H₄₆AsN₂Pd [M – ClO₄]⁺ 843.2851; found

843.2842. Calcd. for [(SIPr)Pd(Allyl)(AsPh₃)]ClO₄ (C₄₈H₅₈AsClN₂O₄Pd): C, 61.09; H, 6.19; N, 2.97%. Found: C, 60.84; H, 5.91; N, 3.22%.

[(IMes)Pd(Allyl)(SbPh₃)]ClO₄ (3e)

The procedure yielded 395 mg (87%) of the pure **3e** as a white powder. ¹H NMR (CDCl₃, 400 MHz) δ (ppm): 7.44 (t, *J* = 7.2 Hz, 3H, *p*-CH-phenyl), 7.36 (t, *J* = 7.2 Hz, 6H, *m*-CH-phenyl), 7.34 (s, 2H, *m*-CH-aniline), 7.04 (d, *J* = 7.2 Hz, 6H, *o*-CH-phenyl), 6.95 (s, 2H, N-CH=CH-N), 6.82 (s, 2H, *m*-CH-aniline), 5.09 (sept, *J* = 6.8 Hz, 1H, CH-allyl), 4.49 (d, *J* = 6.4 Hz, 1H, CH₂-allyl), 3.69 (d, *J* = 6.8 Hz, 1H, CH₂-allyl), 2.62 (d, *J* = 13.2, 1H, CH₂-allyl), 2.27 (d, *J* = 13.6 Hz, 1H, CH₂-allyl), 2.26 (s, 6H, *p*-CH₃-aniline), 2.04 (s, 6H, *o*-CH₃-aniline), 1.80 (s, 6H, *o*-CH₃-aniline).

¹³C NMR (CDCl₃, 100 MHz) δ (ppm): = 178.29 (C_{carbene}), 139.60 (C_{aniline}), 135.22 (C_{phenyl}), 134.34 (C_{aniline}), 131.49 (*o*-C_{phenyl}), 130.61 (C_{aniline}), 129.61 (*p*-C_{phenyl}), 129.57 (*m*-C_{phenyl}), 124.95 (N-CH=CH-N), 118.11 (C_{aniline}), 71.50 (CH-allyl), 64.95 (CH₂-allyl), 20.92 (*p*-CH₃-aniline), 18.40 (*o*-CH₃-aniline), 17.98 (*o*-CH₃-aniline).

HR-MS (ESI): calcd for C₄₂H₄₄N₂PdSb [M – ClO₄]⁺ 803.1578; found 803.1586. Calcd. for [(IMes)Pd(Allyl)(SbPh₃)]ClO₄ (C₄₂H₄₄ClN₂O₄PdSb): C, 55.78; H, 4.90; N, 3.10%. Found: C, 55.56; H, 5.23; N, 3.36%.

[(IPr)Pd(Allyl)(SbPh₃)]ClO₄ (3f)

The procedure yielded 435 mg (88%) of the pure **3f** as a white powder. ¹H NMR (CDCl₃, 400 MHz) δ (ppm): 7.64 (s, 2H, N-CH=CH-N), 7.42 (t, *J* = 7.2 Hz, 3H, *p*-CH-phenyl), 7.35 (t, *J* = 7.6 Hz, 2H, *p*-CH-aniline), 7.31 (t, *J* = 7.2 Hz, 6H, *m*-CH-phenyl), 7.19 (d, *J* = 7.6 Hz, 2H, *m*-CH-aniline), 7.05 (d, *J* = 7.6 Hz, 2H, *m*-CH-aniline), 7.02 (d, *J* = 7.2 Hz, 6H, *m*-CH-phenyl), 4.98 (sept, *J* = 6.4 Hz, 1H, CH-allyl), 4.27 (d, *J* = 5.6 Hz, 1H, CH₂-allyl), 3.64 (d, *J* = 7.2 Hz, 1H, CH₂-allyl), 3.12 (sept, *J* = 6.8 Hz, 2H, CH(CH₃)₂), 2.74 (sept, *J* = 6.8 Hz, 2H, CH(CH₃)₂), 2.24 (d, *J* = 13.6 Hz, 1H, CH₂-allyl), 2.14 (d, *J* = 13.2 Hz, 1H, CH₂-allyl), 1.16 (d, *J* = 6.8 Hz, 6H, CH(CH₃)₂), 1.05 (d, *J* = 6.8 Hz, 6H, CH(CH₃)₂), 1.01 (d, *J* = 6.4 Hz, 6H, CH(CH₃)₂), 0.83 (br, 6H, CH(CH₃)₂). ¹³C NMR (CDCl₃, 100 MHz) δ (ppm): 181.37 (C_{carbene}), 145.22 (C_{aniline}), 145.11 (C_{phenyl}), 135.10 (C_{aniline}), 134.99 (C_{aniline}), 130.86 (*o*-C_{phenyl}), 130.70 (C_{aniline}), 130.63 (C_{aniline}), 129.64 (*p*-C_{phenyl}), 126.85 (*m*-C_{phenyl}),

124.69 (N-CH=CH-N), 124.27 (N-CH=CH-N), 117.63 (C_{aniline}), 71.65 (CH-allyl), 66.81 (CH₂-allyl), 28.82 (CH(CH₃)₂), 28.51 (CH(CH₃)₂), 26.82 (CH(CH₃)₂), 25.74 (CH(CH₃)₂), 22.61 (CH(CH₃)₂), 22.53 (CH(CH₃)₂). HR-MS (ESI): calcd for C₄₈H₅₆N₂PdSb [M - ClO₄]⁺ 887.2517; found 887.2529. Calcd. for [(IPr)Pd(Allyl)(SbPh₃)]ClO₄ (C₄₈H₅₆ClN₂O₄PdSb): C, 58.32; H, 5.71; N, 2.83%. Found: C, 58.58; H, 5.96; N, 3.15%.

[(SImes)Pd(Allyl)(SbPh₃)]ClO₄ (**3g**)

The procedure yielded 412 mg (91%) of the pure **3g** as a white powder. ¹H NMR (CDCl₃, 400 MHz) δ (ppm): 7.43 (t, $J = 7.2$ Hz, 3H, *p*-CH-phenyl), 7.35 (t, 6H, $J = 7.2$ Hz, *m*-CH-phenyl), 7.02 (d, $J = 7.2$ Hz, 6H, *o*-CH-phenyl), 6.87 (br, 2H, *m*-CH-aniline), 6.58 (br, 2H, *m*-CH-aniline), 4.94 (sept, $J = 6.8$ Hz, 1H, CH-allyl), 4.60 (d, $J = 6.4$ Hz, 1H, CH₂-allyl), 4.15 (s, 4H, N-CH₂-CH₂-N), 3.52 (d, $J = 7.2$ Hz, 1H, CH₂-allyl), 2.61 (d, $J = 13.2$ Hz, 1H, CH₂-allyl), 2.22 (s, 12H, *o*-CH₃-aniline), 2.13 (d, $J = 13.2$ Hz, 1H, CH₂-allyl), 1.68 (s, 6H, *p*-CH₃-aniline). ¹³C NMR (CDCl₃, 100 MHz) δ (ppm): 207.83 (C_{carbene}), 138.47 (C_{aniline}), 135.27 (C_{phenyl}), 135.16 (C_{aniline}), 131.46 (*o*-C_{phenyl}), 130.50 (C_{aniline}), 129.52 (*p*-C_{phenyl}), 129.44 (*m*-C_{phenyl}), 117.92 (C_{aniline}), 70.94 (CH-allyl), 65.41 (CH₂-allyl), 51.89 (N-CH₂-CH₂-N), 20.77 (*p*-CH₃-aniline), 17.84 (*o*-CH₃-aniline). HR-MS (ESI): calcd for C₄₂H₄₆N₂PdSb [M - ClO₄]⁺ 805.1734; found 805.1725. Calcd. for [(SImes)Pd(Allyl)(SbPh₃)]ClO₄ (C₄₂H₄₆ClN₂O₄PdSb): C, 55.65; H, 5.12; N, 3.09%. Found: C, 55.87; H, 5.37; N, 3.26%.

[(SIPr)Pd(Allyl)(SbPh₃)]ClO₄ (**3h**)

The procedure yielded 420 mg (85%) of the pure **3h** as a white powder. ¹H NMR (CDCl₃, 400 MHz) δ (ppm): 7.41 (t, $J = 7.2$ Hz, 3H, *p*-CH-phenyl), 7.34 (t, 6H, $J = 7.2$ Hz, *m*-CH-phenyl), 7.23 (t, $J = 7.6$ Hz, 2H, *p*-CH-aniline), 7.12–7.11 (m, 8H, *o*-CH-phenyl and *m*-CH-aniline), 6.98 (br, 2H, *m*-CH-aniline), 4.88 (sept, $J = 6.8$ Hz, 1H, CH-allyl), 4.45 (s, 4H, N-CH₂-CH₂-N), 4.21 (d, $J = 6.4$ Hz, 1H, CH₂-allyl), 3.55 (d, $J = 7.2$ Hz, 1H, CH₂-allyl), 3.43 (br, 2H, CH(CH₃)₂), 3.28 (sept, $J = 6.4$ Hz, 2H, CH(CH₃)₂), 2.03 (d, $J = 13.2$ Hz, 1H, CH₂-allyl), 1.98 (d, $J = 13.6$ Hz, 1H, CH₂-allyl), 1.22 (br, 6H, CH(CH₃)₂), 1.18 (d, $J = 6.4$ Hz, 12H, CH(CH₃)₂), 1.02 (br, 6H,

CH(CH₃)₂). ¹³C NMR (CDCl₃, 100 MHz) δ (ppm): 210.27 (C_{carbene}), 146.46 (C_{aniline}), 146.38 (C_{aniline}), 135.77 (C_{phenyl}), 135.15 (C_{aniline}), 130.88 (*o*-C_{phenyl}), 130.60 (C_{aniline}), 129.80 (*p*-C_{phenyl}), 129.60 (*m*-C_{phenyl}), 124.83 (C_{aniline}), 124.42 (C_{aniline}), 117.64 (C_{aniline}), 71.40 (CH-allyl), 67.07 (CH₂-allyl), 55.27 (N-CH₂-CH₂-N), 28.72 (CH(CH₃)₂), 28.38 (CH(CH₃)₂), 26.93 (CH(CH₃)₂), 26.57 (CH(CH₃)₂), 23.58 (CH(CH₃)₂), 23.16 (CH(CH₃)₂). HR-MS (ESI): calcd for C₄₈H₅₈N₂PdSb [M - ClO₄]⁺ 887.2517; found 887.2529. Calcd. for [(SIPr)Pd(Allyl)(SbPh₃)]ClO₄ (C₄₈H₅₈ClN₂O₄PdSb): C, 58.20; H, 5.90; N, 2.83%. Found: C, 58.47; H, 6.24; N, 3.19%.

4.3 General procedure for [(NHC)Pd(Allyl)(EPh₃)]ClO₄ (E =As or Sb) catalyzed Sonogashira coupling reaction

A Schlenk tube containing a stirring bar was charged with aryl bromide (0.5 mmol), terminal alkyne (0.6 mmol), [(NHC)Pd(Allyl)(EPh₃)]ClO₄ (0.005 mmol), Cs₂CO₃ (0.6 mmol) and DMF (2.0 mL) under air. The mixture was stirred at 100 °C for 6 h. After completion of the reaction, the filtrate was concentrated and the residue was subjected to purification *via* column chromatography to give the corresponding product.

4.5 X-Ray crystallography

Data collection was performed on a Bruker-AXS SMART CMOS area detector diffractometer at 296 K using ω rotation scans with a scan width of 0.5° and Mo-K α radiation ($\lambda = 0.71073$ Å). Multi-scan corrections were applied using *SADABS*.^[12] Structure solutions and refinements were performed with the *SHELX-2014* package.^[13] All non-hydrogen atoms were refined anisotropically by full-matrix least-squares on F^2 . The hydrogen atoms to carbon were included in idealized geometric positions with thermal parameters equivalent to 1.2 times those of carbon atoms. A summary of the crystallographic data, data collection, and refinement parameters for complexes **3a–3h** were provided in Table S1. CCDC 1880562–1880569 contain the supplementary crystallographic data for this paper.

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Highlights

- □ Triphenylarsine and triphenylstibine-stabilized tri-heteroleptic NHC–Pd–allyl complexes were synthesized.
- Molecular structures have been elucidated by X-ray single-crystal diffraction.
- The catalytic activities of the complexes were examined in Sonogashira coupling reaction.