Journal of Organometallic Chemistry 883 (2019) 35–40

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

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

Jin Yang

Department of Chemistry, Huaibei Normal University, Huaibei, Anhui, 235000, PR China

ARTICLE INFO

Article history:
Received 7 December 2018
Received in revised form
9 January 2019
Accepted 16 January 2019
Available online 17 January 2019

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

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.

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)$PdCl_2(EPh_3)$ (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 $[(NHC)Pd(allyl)(EPh_3)]ClO_4$ (E = As, Sb) (**3a–3h**) and their further utility in Sonogashira coupling reaction.

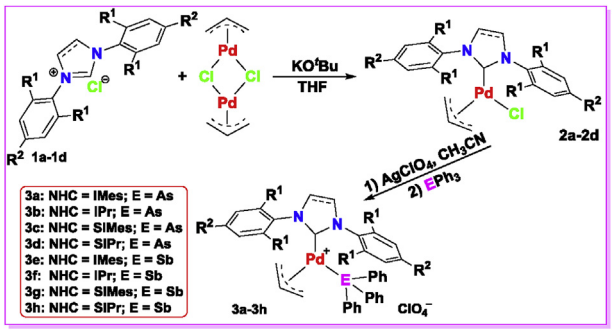
2. Results and discussion

2.1. Synthesis of the $[(NHC)Pd(allyl)(EPh_3)]ClO_4$ (E = As, Sb) complexes

The $[(NHC)Pd(allyl)(EPh_3)]ClO_4$ complexes were prepared in one pot based on anion metathesis and then ligand replacement with EPh_3 (NHC: IMes = *N*,*N*′-bis- (2,4,6-trimethylphenyl)imidazole-2-ylidene; IPr = *N*,*N*′-bis- (2,6-di(isopropyl)phenyl)imidazole-2-ylidene; SIMes = *N*,*N*′-bis- (2,4,6-trimethylphenyl)imidazolidin-2-

E-mail address: yangjinlz@163.com.

https://doi.org/10.1016/j.jorganchem.2019.01.011
0022-328X/



Scheme 1. Synthesis of the well-defined tri-heteroleptic NHC–Pd–allyl complexes [(NHC)Pd(allyl)(EPh$_3$)]ClO$_4$ (E = As, Sb) (**3a–3h**).

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^{t}Bu in dry THF [7]. The anion metathesis of (NHC)Pd(allyl)Cl with AgClO$_4$ in CH$_3$CN generated the solvated complexes [(NHC)Pd(allyl)(CH$_3$CN)]ClO$_4$ (**2a–2d**) in almost quantitative yields. The obtained complexes subsequently reacted with EPh$_3$ through ligand replacement to afford the above-mentioned products (**3a–3h**). Complexes **3a–3h** have been fully characterized by ^{1}H NMR, ^{13}C 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 EPh$_3$ in ^{1}H NMR spectra. Furthermore, the ^{13}C NMR spectra revealed the appearance of the carbonic carbons as diagnostic singlet peaks (178.29-181.54 ppm for IMes and IPr-bearing complexes; 207.83-210.37 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 Fig. 1. In all cases the common distorted square-planar coordination around the palladium centre with an environment of an NHC, the allyl moiety and an As or Sb donor was observed. The allyl moiety is η^3-coordinated to the palladium with one terminal carbon *trans* to the carbene and the second terminal carbon *trans* to EPh$_3$. 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.

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$_2$CO$_3$ as base gave the best yield at 100 °C in 6 h (Table 1, entry 1). Under the same conditions, using K$_2$CO$_3$ as the base could also give a similar result. However, other inorganic bases, like Na$_2$CO$_3$, KHCO$_3$, KOH and KO^{t}Bu 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 [(NHC)Pd(allyl)(EPh$_3$)]ClO$_4$ and remain stable in DMF or DMA. However, in the presence of other solvents such as

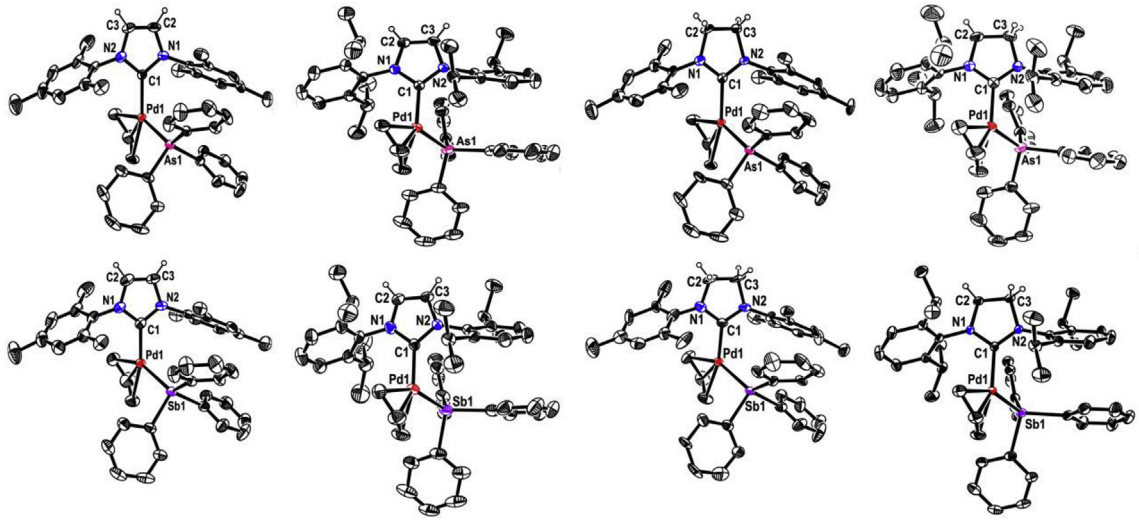


Fig. 1. ORTEP diagrams of complexes **3a–3h** with thermal displacement parameters drawn at 30% probability. The anions (ClO$_4^-$), solvent molecules (CH$_2$Cl$_2$ or CHCl$_3$) and parts of the hydrogen atoms have been omitted for clarity.

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_2CO_3	91
2	**3b** (1.0%)	DMF	K_2CO_3	87
3	**3b** (1.0%)	DMF	Na_2CO_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_2CO_3	88
8	**3b** (1.0%)	DMSO	Cs_2CO_3	65
9	**3b** (1.0%)	1,4-dioxane	Cs_2CO_3	20
10	**3b** (1.0%)	CH_3CN	Cs_2CO_3	trace
11	**3b** (1.0%)	THF	Cs_2CO_3	trace
12	**3b** (0.5%)	DMF	Cs_2CO_3	65
13[c]	**3b** (0.5%)	DMF	Cs_2CO_3	72
14[d]	**3b** (1.0%)	DMF	Cs_2CO_3	80
15[e]	**3b** (1.0%)	DMF	Cs_2CO_3	72
16[f]	**3b** (1.0%)	DMF	Cs_2CO_3	92
17[g]	**3b** (1.0%)	DMF	Cs_2CO_3	54
18	**3a** (1.0%)	DMF	Cs_2CO_3	50
19	**3c** (1.0%)	DMF	Cs_2CO_3	42
20	**3d** (1.0%)	DMF	Cs_2CO_3	90
21	**3e** (1.0%)	DMF	Cs_2CO_3	40
22	**3f** (1.0%)	DMF	Cs_2CO_3	88
23	**3g** (1.0%)	DMF	Cs_2CO_3	35
24	**3h** (1.0%)	DMF	Cs_2CO_3	85

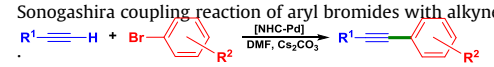
[a] Reaction conditions: 4-bromoanisole (0.5 mmol), phenylacetylene (0.6 mmol), complex **3b** (0.005 mmol), base (0.6 mmol), solvent (2.0 mL), 100 °C, 6 h.
[b] Isolated yield.
[c] Reaction time is 12 h.
[d] Reaction temperature is 130 °C.
[e] Reaction temperature is 80 °C.
[f] Under nitrogen atmosphere.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

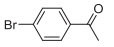
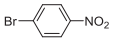
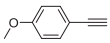
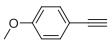
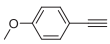
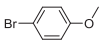
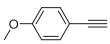
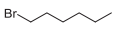
DMSO, moderate yield was obtained. When 1,4-dioxane, CH_3CN and THF were used, no reaction occurred. The catalyst loading and reaction temperature were then tested. When the catalyst loading was reduced to 0.5 mol%, the yield lowered to 65% (Entry 12). However, the yields could be increased slightly 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.

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

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), Cs_2CO_3 (0.6 mmol), DMF (2.0 mL) at 100 °C for 6 h.
[b] Isolated yield.

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.

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 ^{1}H NMR) and 100 MHz (for ^{13}C NMR) on a Bruker Avance 400 NMR spectrometer. All ^{1}H, 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 elementar. 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.

4.2.1. [(IMes)Pd(Allyl)(AsPh$_3$)]ClO$_4$ (**3a**)

The procedure yielded 385 mg (90%) of the pure **3a** as a white powder. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) = 7.43 (t, J = 7.2 Hz, 3H, *p*-C*H*-phenyl), 7.34 (s, 2H, *m*-C*H*-aniline), 7.32 (t, J = 7.2 Hz, 6H, *m*-C*H*-phenyl), 6.96 (br, 4H, N–C*H*=C*H*–N and *m*-C*H*-aniline), 6.90 (d, J = 6.8 Hz, 6H, *o*-C*H*-phenyl), 5.08 (sept, J = 6.8 Hz, 1H, C*H*-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–C*H*=C*H*–N), 119.01 ($C_{aniline}$), 71.04 (*C*H-allyl), 67.59 (*C*H_2-allyl), 20.89 (*p*-*C*H_3-aniline), 18.36 (*o*-*C*H_3-aniline), 18.02 (*o*-*C*H_3-aniline). HR-MS (ESI): calcd for $C_{42}H_{44}AsN_2Pd$ [M − ClO_4^-]$^+$ 757.1755; found 757.1784. Calcd. for [(IMes)Pd(Allyl)($AsPh_3$)]ClO_4 ($C_{42}H_{44}AsClN_2O_4Pd$): C, 58.82; H, 5.17; N, 3.27%. Found: C, 58.55; H, 5.33; N, 3.56%.

4.2.2. [(IPr)Pd(Allyl)(AsPh$_3$)]ClO$_4$ (**3b**)

The procedure yielded 410 mg (87%) of the pure **3b** as a white powder. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.61 (s, 2H, N–C*H*=C*H*–N), 7.41 (t, J = 7.0 Hz, 3H, *p*-C*H*-phenyl), 7.29 (t, J = 7.5 Hz, 6H, *m*-C*H*-phenyl), 7.27–7.26 (m, 2H, *p*-C*H*-aniline), 7.18 (br, 3H, *m*-C*H*-aniline), 6.93 (d, J = 6.0 Hz, 6H, *m*-C*H*-phenyl), 6.73 (br, 1H, *m*-C*H*-aniline), 5.13 (sept, J = 6.5 Hz, 1H, C*H*-allyl), 4.27 (d, J = 7.0 Hz, 1H, CH_2-allyl), 3.29 (d, J = 7.5 Hz, 1H, CH_2-allyl), 2.96 (br, 2H, C*H*$(CH_3)_2$), 2.52 (br, 2H, C*H*$(CH_3)_2$), 2.29 (d, J = 13.5 Hz, 1H, CH_2-allyl), 2.09 (d, J = 13.0 Hz, 1H, CH_2-allyl), 1.32 (br, 6H, CH(CH_3)$_2$), 1.15 (br, 6H, CH(CH_3)$_2$), 1.02 (br, 6H, CH(CH_3)$_2$), 0.70 (br, 3H, CH(CH_3)$_2$), 0.24 (br, 3H, CH(CH_3)$_2$). ^{13}C NMR ($CDCl_3$, 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–C*H*=C*H*–N), 119.19 ($C_{aniline}$), 73.11 (*C*H-allyl), 67.95 (*C*H_2-allyl), 28.72 (*C*H$(CH_3)_2$), 28.50 (CH(*C*H_3)$_2$), 26.96 (CH(*C*H_3)$_2$), 25.73 (CH(*C*H_3)$_2$), 22.60 (CH(*C*H_3)$_2$), 22.52 (CH(*C*H_3)$_2$). HR-MS (ESI): calcd for $C_{48}H_{56}AsN_2Pd$ [M − ClO_4^-]$^+$ 841.2694; found 841.2687. Calcd. for [(IPr)Pd(Allyl)($AsPh_3$)]ClO_4 ($C_{48}H_{56}AsClN_2O_4Pd$): C, 61.22; H, 5.99; N, 2.97%. Found: C, 60.96; H, 5.73; N, 3.18%.

4.2.3. [(SIMes)Pd(Allyl)(AsPh$_3$)]ClO$_4$ (**3c**)

The procedure yielded 390 mg (91%) of the pure **3c** as a white powder. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.42 (t, J = 7.2 Hz, 3H, *p*-C*H*-phenyl), 7.32 (t, J = 7.6 Hz, 6H, *m*-C*H*-phenyl), 7.00 (s, 1H, *m*-C*H*-aniline), 6.96 (s, 1H, *m*-C*H*-aniline), 6.89 (d, J = 7.6 Hz, 6H, *o*-C*H*-phenyl), 6.80 (s, 1H, *m*-C*H*-aniline), 6.51 (s, 1H, *m*-C*H*-aniline), 4.93 (sept, J = 6.8 Hz, 1H, C*H*-allyl), 4.33 (d, J = 6.4 Hz, 1H, CH_2-allyl), 4.15 (s, 4H, N–CH_2–CH_2–N), 3.19 (d, J = 7.2 Hz, 1H, CH_2-allyl), 2.42 (s, 3H, *o*-CH_3-aniline), 2.40 (d, J = 13.2, 1H, CH_2-allyl), 2.31 (s, 6H, *p*-CH_3-aniline), 2.23 (s, 3H, *o*-CH_3-aniline), 2.16 (d, J = 13.2 Hz, 1H, CH_2-allyl), 2.02 (s, 3H, *o*-CH_3-aniline), 1.64 (s, 3H, *o*-CH_3-aniline). ^{13}C NMR ($CDCl_3$, 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 (*C*H-allyl), 67.33 (*C*H_2-allyl), 52.17 (N–*C*H_2–*C*H_2–N), 51.99 (N–*C*H_2–*C*H_2–N), 20.92 (*p*-*C*H_3-aniline), 18.69 (*o*-*C*H_3-aniline), 18.19 (*o*-*C*H_3-aniline), 18.09 (*o*-*C*H_3-aniline), 17.84 (*o*-*C*H_3-aniline). HR-MS (ESI): calcd for $C_{42}H_{46}AsN_2Pd$ [M − ClO_4^-]$^+$ 759.1912; found 759.1923. Calcd. for [(SIMes)Pd(Allyl)($AsPh_3$)]ClO_4 ($C_{42}H_{46}AsClN_2O_4Pd$): C, 58.68; H, 5.39; N, 3.26%. Found: C, 58.94; H, 5.21; N, 3.49%.

4.2.4. [(SIPr)Pd(Allyl)(AsPh$_3$)]ClO$_4$ (**3d**)

The procedure yielded 420 mg (89%) of the pure **3d** as a white powder. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.42 (t, J = 7.0 Hz, 3H, *p*-C*H*-phenyl), 7.34 (br, 6H, *m*-C*H*-phenyl), 7.28 (t, J = 7.0 Hz, 2H, *p*-

C*H*-aniline), 7.19–7.17 (m, 2H, *m*-C*H*-aniline), 7.12 (t, $J = 7.5$ Hz, 2H, *o*-C*H*-phenyl), 7.12 (br, 3H, *o*-C*H*-phenyl), 7.01–7.00 (br, 2H, *m*-C*H*-aniline), 6.61 (d, $J = 7.5$ Hz, 1H, *o*-C*H*-phenyl), 5.01 (sept, $J = 6.5$ Hz, 1H, C*H*-allyl), 4.68 (q, $J = 11.0$ Hz, 1H, N–CH_2–CH_2–N), 4.59 (td, $J = 11.0$ and 5.5 Hz, 1H, N–CH_2–CH_2–N), 4.26 (td, $J = 11.0$ and 5.5 Hz, 1H, N–CH_2–CH_2–N), 4.09 (q, $J = 11.0$ Hz, 1H, N–CH_2–⊖ CH_2–N), 4.01 (d, $J = 7.0$ Hz, 1H, CH_2-allyl), 3.51 (sept, $J = 6.5$ Hz, 1H, CH(CH_3)$_2$), 3.34 (sept, $J = 6.5$ Hz, 2H, CH(CH_3)$_2$), 3.22 (sept, $J = 6.5$ Hz, 1H, CH(CH_3)$_2$), 3.18 (d, $J = 7.0$ Hz, 1H, CH_2-allyl), 2.23 (d, $J = 13.5$ Hz, 1H, CH_2-allyl), 1.86 (d, $J = 13.0$ Hz, 1H, CH_2-allyl), 1.49 (d, $J = 6.5$ Hz, 3H, CH(CH_3)$_2$), 1.36 (d, $J = 6.5$ Hz, 3H, CH(CH_3)$_2$), 1.34 (d, $J = 7.0$ Hz, 3H, CH(CH_3)$_2$), 1.24 (d, $J = 7.0$ Hz, 3H, CH(CH_3)$_2$), 1.11 (d, $J = 6.5$ Hz, 3H, CH(CH_3)$_2$), 1.07 (d, $J = 6.5$ Hz, 3H, CH(CH_3)$_2$), 0.71 (d, $J = 6.5$ Hz, 3H, CH(CH_3)$_2$), 0.19 (d, $J = 6.5$ Hz, 3H, CH(CH_3)$_2$). ^{13}C NMR (CDCl$_3$, 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 (*C*H-allyl), 67.37 (*C*H$_2$-allyl), 55.63 (N–*C*H$_2$–*C*H$_2$–N), 55.19 (N–*C*H$_2$–*C*H$_2$–N), 28.97 (*C*H(CH$_3$)$_2$), 28.62 (*C*H(CH$_3$)$_2$), 28.50 (*C*H(CH$_3$)$_2$), 28.30 (*C*H(CH$_3$)$_2$), 27.09 (CH(*C*H$_3$)$_2$), 27.03 (CH(*C*H$_3$)$_2$), 26.94 (CH(*C*H$_3$)$_2$), 26.23 (CH(*C*H$_3$)$_2$), 23.84 (CH(*C*H$_3$)$_2$), 23.75 (CH(*C*H$_3$)$_2$), 23.35 (CH(*C*H$_3$)$_2$), 22.54 (CH(*C*H$_3$)$_2$). HR-MS (ESI): calcd for $C_{42}H_{46}AsN_2Pd$ [M − ClO_4^-]$^+$ 843.2851; found 843.2842. Calcd. for [(SIPr)Pd(Allyl)(AsPh$_3$)]ClO_4 ($C_{48}H_{58}AsClN_2O_4Pd$): C, 61.09; H, 6.19; N, 2.97%. Found: C, 60.84; H, 5.91; N, 3.22%.

4.2.5. [(IMes)Pd(Allyl)(SbPh$_3$)]ClO_4 (**3e**)

The procedure yielded 395 mg (87%) of the pure **3e** as a white powder. ^{1}H NMR (CDCl$_3$, 400 MHz) δ (ppm): 7.44 (t, $J = 7.2$ Hz, 3H, *p*-C*H*-phenyl), 7.36 (t, $J = 7.2$ Hz, 6H, *m*-C*H*-phenyl), 7.34 (s, 2H, *m*-C*H*-aniline), 7.04 (d, $J = 7.2$ Hz, 6H, *o*-C*H*-phenyl), 6.95 (s, 2H, N–C*H*=C*H*–N), 6.82 (s, 2H, *m*-C*H*-aniline), 5.09 (sept, $J = 6.8$ Hz, 1H, C*H*-allyl), 4.49 (d, $J = 6.4$ Hz, 1H, CH_2-allyl), 3.69 (d, $J = 6.8$ Hz, 1H, CH_2-allyl), 2.62 (d, $J = 13.2$, 1H, CH_2-allyl), 2.27 (d, $J = 13.6$ Hz, 1H, CH_2-allyl), 2.26 (s, 6H, *p*-CH_3-aniline), 2.04 (s, 6H, *o*-CH_3-aniline), 1.80 (s, 6H, *o*-CH_3-aniline).

^{13}C NMR (CDCl$_3$, 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–*C*H=*C*H–N), 118.11 ($C_{aniline}$), 71.50 (*C*H-allyl), 64.95 (*C*H$_2$-allyl), 20.92 (*p*-CH_3-aniline), 18.40 (*o*-CH_3-aniline), 17.98 (*o*-CH_3-aniline). HR-MS (ESI): calcd for $C_{42}H_{44}N_2PdSb$ [M − ClO_4^-]$^+$ 803.1578; found 803.1586. Calcd. for [(IMes)Pd(Allyl)(SbPh$_3$)]ClO_4 ($C_{42}H_{44}ClN_2O_4PdSb$): C, 55.78; H, 4.90; N, 3.10%. Found: C, 55.56; H, 5.23; N, 3.36%.

4.2.6. [(IPr)Pd(Allyl)(SbPh$_3$)]ClO_4 (**3f**)

The procedure yielded 435 mg (88%) of the pure **3f** as a white powder. ^{1}H NMR (CDCl$_3$, 400 MHz) δ (ppm): 7.64 (s, 2H, N–C*H*=C*H*–N), 7.42 (t, $J = 7.2$ Hz, 3H, *p*-C*H*-phenyl), 7.35 (t, $J = 7.6$ Hz, 2H, *p*-C*H*-aniline), 7.31 (t, $J = 7.2$ Hz, 6H, *m*-C*H*-phenyl), 7.19 (d, $J = 7.6$ Hz, 2H, *m*-C*H*-aniline), 7.05 (d, $J = 7.6$ Hz, 2H, *m*-C*H*-aniline), 7.02 (d, $J = 7.2$ Hz, 6H, *m*-C*H*-phenyl), 4.98 (sept, $J = 6.4$ Hz, 1H, C*H*-allyl), 4.27 (d, $J = 5.6$ Hz, 1H, CH_2-allyl), 3.64 (d, $J = 7.2$ Hz, 1H, CH_2-allyl), 3.12 (sept, $J = 6.8$ Hz, 2H, CH(CH$_3$)$_2$), 2.74 (sept, $J = 6.8$ Hz, 2H, CH(CH$_3$)$_2$), 2.24 (d, $J = 13.6$ Hz, 1H, CH_2-allyl), 2.14 (d, $J = 13.2$ Hz, 1H, CH_2-allyl), 1.16 (d, $J = 6.8$ Hz, 6H, CH(CH_3)$_2$), 1.05 (d, $J = 6.8$ Hz, 6H, CH(CH_3)$_2$), 1.01 (d, $J = 6.4$ Hz, 6H, CH(CH_3)$_2$). 0.83 (br, 6H, CH(CH_3)$_2$). ^{13}C NMR (CDCl$_3$, 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–*C*H=*C*H–N), 124.27 (N–*C*H=*C*H–N), 117.63 ($C_{aniline}$), 71.65 (*C*H-allyl), 66.81 (*C*H$_2$-allyl), 28.82 (*C*H(CH$_3$)$_2$), 28.51 (*C*H(CH$_3$)$_2$), 26.82 (CH(*C*H$_3$)$_2$), 25.74 (CH(*C*H$_3$)$_2$), 22.61 (CH(*C*H$_3$)$_2$), 22.53 (CH(*C*H$_3$)$_2$). HR-MS (ESI): calcd for $C_{48}H_{56}N_2PdSb$ [M − ClO_4^-]$^+$ 887.2517; found 887.2529. Calcd. for [(IPr)Pd(Allyl)(SbPh$_3$)]ClO_4 ($C_{48}H_{56}ClN_2O_4PdSb$): C, 58.32; H, 5.71; N, 2.83%. Found: C, 58.58; H, 5.96; N, 3.15%.

4.2.7. [(SIMes)Pd(Allyl)(SbPh$_3$)]ClO_4 (**3g**)

The procedure yielded 412 mg (91%) of the pure **3g** as a white powder. ^{1}H NMR (CDCl$_3$, 400 MHz) δ (ppm): 7.43 (t, $J = 7.2$ Hz, 3H, *p*-C*H*-phenyl), 7.35 (t, 6H, $J = 7.2$ Hz, *m*-C*H*-phenyl), 7.02 (d, $J = 7.2$ Hz, 6H, *o*-C*H*-phenyl), 6.87 (br, 2H, *m*-C*H*-aniline), 6.58 (br, 2H, *m*-C*H*-aniline), 4.94 (sept, $J = 6.8$ Hz, 1H, C*H*-allyl), 4.60 (d, $J = 6.4$ Hz, 1H, CH_2-allyl), 4.15 (s, 4H, N–CH_2–CH_2–N), 3.52 (d, $J = 7.2$ Hz, 1H, CH_2-allyl), 2.61 (d, $J = 13.2$ Hz, 1H, CH_2-allyl), 2.22 (s, 12H, *o*-CH_3-aniline), 2.13 (d, $J = 13.2$ Hz, 1H, CH_2-allyl), 1.68 (s, 6H, *p*-CH_3-aniline). ^{13}C NMR (CDCl$_3$, 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 (*C*H-allyl), 65.41 (*C*H$_2$-allyl), 51.89 (N–CH$_2$–CH$_2$–N), 20.77 (*p*-CH$_3$-aniline), 17.84 (*o*-CH$_3$-aniline). HR-MS (ESI): calcd for $C_{42}H_{46}N_2PdSb$ [M − ClO_4^-]$^+$ 805.1734; found 805.1725. Calcd. for [(SIMes)Pd(Allyl)(SbPh$_3$)]ClO_4 ($C_{42}H_{46}ClN_2O_4PdSb$): C, 55.65; H, 5.12; N, 3.09%. Found: C, 55.87; H, 5.37; N, 3.26%.

4.2.8. [(SIPr)Pd(Allyl)(SbPh$_3$)]ClO_4 (**3h**)

The procedure yielded 420 mg (85%) of the pure **3h** as a white powder. ^{1}H NMR (CDCl$_3$, 400 MHz) δ (ppm): 7.41 (t, $J = 7.2$ Hz, 3H, *p*-C*H*-phenyl), 7.34 (t, 6H, $J = 7.2$ Hz, *m*-C*H*-phenyl), 7.23 (t, $J = 7.6$ Hz, 2H, *p*-C*H*-aniline), 7.12–7.11 (m, 8H, *o*-C*H*-phenyl and *m*-C*H*-aniline), 6.98 (br, 2H, *m*-C*H*-aniline), 4.88 (sept, $J = 6.8$ Hz, 1H, C*H*-allyl), 4.45 (s, 4H, N–CH_2–CH_2–N), 4.21 (d, $J = 6.4$ Hz, 1H, CH_2-allyl), 3.55 (d, $J = 7.2$ Hz, 1H, CH_2-allyl), 3.43 (br, 2H, CH(CH$_3$)$_2$), 3.28 (sept, $J = 6.4$ Hz, 2H, CH(CH$_3$)$_2$), 2.03 (d, $J = 13.2$ Hz, 1H, CH_2-allyl), 1.98 (d, $J = 13.6$ Hz, 1H, CH_2-allyl), 1.22 (br, 6H, CH(CH_3)$_2$), 1.18 (d, $J = 6.4$ Hz, 12H, CH(CH_3)$_2$), 1.02 (br, 6H, CH(CH_3)$_2$). ^{13}C NMR (CDCl$_3$, 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 (*C*H-allyl), 67.07 (*C*H$_2$-allyl), 55.27 (N–*C*H$_2$–*C*H$_2$–N), 28.72 (*C*H(CH$_3$)$_2$), 28.38 (*C*H(CH$_3$)$_2$), 26.93 (CH(*C*H$_3$)$_2$), 26.57 (CH(*C*H$_3$)$_2$), 23.58(CH(*C*H$_3$)$_2$), 23.16(CH(*C*H$_3$)$_2$). HR-MS (ESI): calcd for $C_{48}H_{58}N_2PdSb$ [M − ClO_4^-]$^+$ 887.2517; found 887.2529. Calcd. for [(SIPr)Pd(Allyl)(SbPh$_3$)]ClO_4 ($C_{48}H_{58}ClN_2O_4PdSb$): 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)(EPh$_3$)]ClO_4 (E = As or Sb) catalyzed Sonogashira coupling reaction

A Schlenck tube containing a stirring bar was charged with aryl bromide (0.5 mmol), terminal alkyne (0.6 mmol), [(NHC)Pd(Allyl)(EPh$_3$)]ClO_4 (0.005 mmol), Cs_2CO_3 (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.

4.4. 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-Kα 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.

Acknowledgments

Financial support from the Scientific Research Project of Anhui Provincial Education Department (KJ2015TD002) is gratefully acknowledged.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jorganchem.2019.01.011.

References

[1] G.A. Lawrance, Introduction to Coordination Chemistry, John Wiley & Sons, Ltd, 2010.
[2] (a) *N*-heterocyclic carbenes in transition metal catalysis, in: F. Glorius (Ed.), Topics in Organometallic Chemistry, vol. 21, Springer-Verlag, Berlin, 2007;
(b) (*N*-Heterocyclic Carbene)–palladium complexes in catalysis, in: S.P. Nolan (Ed.), *N*-heterocyclic Carbenes: Effective Tools for Organometallic Synthesis, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2014;
(c) G.C. Fortmana, S.P. Nolan, Chem. Soc. Rev. 40 (2011) 5151–5169;
(d) N. Gürbüz, E.Ö. Karaca, İ. Özdemir, B. Çetinkaya, Turk. J. Chem. 39 (2015) 1115–1157.
[3] (a) M.S. Viciu, R.A. Kelly III, E.D. Stevens, F. Naud, M. Studer, S.P. Nolan, Org. Lett. 5 (2003) 1479–1482;
(b) N. Marion, O. Navarro, J. Mei, E.D. Stevens, N.M. Scott, S.P. Nolan, J. Am. Chem. Soc. 128 (2006) 4101–4111;
(c) O.H. Winkelmann, A. Riekstins, S.P. Nolan, O. Navarro, Organometallics 28 (2009) 5809–5813;
(d) M.G. Organ, S. Avola, I. Dubovyk, N. Hadei, E.A.B. Kantchev, C.J. O'Brien, C. Valente, Chem. Eur J. 12 (2006) 4749–4755.
[4] (For selected example): (a) O. Kaufhold, A. Stasch, T. Pape, A. Hepp, P.G. Edwards, P.D. Newman, F.E. Hahn, J. Am. Chem. Soc. 131 (2009) 306–317;
(b) O. Diebolt, V. Jurcik, R. Correa da Costa, P. Braunstein, L. Cavallo, S.P. Nolan, A.M.Z. Slawin, C.S.J. Cazin, Organometallics 29 (2010) 1443–1450;
(c) S. Gaillard, J.-L. Renaud, Dalton Trans. 42 (2013) 7255–7270;
(d) T.E. Schmid, D.C. Jones, O. Songis, O. Diebolt, M.R.L. Furst, A.M.Z. Slawin, C.S.J. Cazin, Dalton Trans. 42 (2013) 7345–7353;
(e) J. Yang, P. Li, Y. Zhang, L. Wang, Dalton Trans. 43 (2014) 7166–7175;
(f) J. Yang, P. Li, Y. Zhang, L. Wang, J. Organomet. Chem. 766 (2014) 73–78;
(g) S. Modak, M.K. Gangwar, M.,N. Rao, M. Madasu, A.C. Kalita, V. Dorcet, M.A. Shejale, R.J. Butcherc, P. Ghosh, Dalton Trans. 44 (2015) 17617–17628;
(h) L. Boubakri, S. Yasar, V. Dorcet, T. Roisnel, C. Bruneau, N. Hamdib, I. Ozdemira, New J. Chem. 41 (2017) 51053–55113;
(i) Z.I. Dehimat, S. Yaşar, D. Tebbani, İ. Özdemir, Inorg. Chim. Acta. 469 (2018) 325–334;
(j) N. Touj, S. Yaşar, N. Özdemir, N. Hamdi, İ. Özdemir, J. Organomet. Chem. 860 (2018) 59–71;
(k) L. Boubakri, L. Mansour, A.H. Harrath, I. Özdemir, S. Yaşar, N. Hamdi, J. Coord. Chem. 71 (2018) 183–199.
[5] A.T. Normand, A. Stasch, L.-L. Ooi, K.J. Cavell, Organometallics 27 (2008) 6507–6520.
[6] J. Yang, P. Li, Y. Zhang, L. Wang, Dalton Trans. 43 (2014) 14114–14122.
[7] M.S. Viciu, R.F. Germaneau, O. Navarro-Fernandez, E.D. Stevens, S.P. Nolan, Organometallics 21 (2002) 5470–5472.
[8] (a) R. Chinchilla, C. Nájera, Chem. Rev. 107 (2007) 874–922;
(b) R. Chinchilla, C. Nájera, Chem. Soc. Rev. 40 (2011) 5084–5121;
(c) M. García-Melchor, A.A.C. Braga, A. Lledós, G. Ujaque, F. Maseras, Acc. Chem. Res. 46 (2013) 2626–2634.
[9] (a) M.K. Samantaray, M.M. Shaikh, P. Ghosh, J. Organomet. Chem. 694 (2009) 3477–3486;
(b) L. Yang, P. Guan, P. He, Q. Chen, C. Cao, Y. Peng, Z. Shi, G. Pang, Y. Shi, Dalton Trans. 41 (2012) 5020–5025;
(c) H.V. Huynh, C.-S. Lee, Dalton Trans. 42 (2013) 6803–6809;
(d) P. Dubey, S. Gupta, A.K. Singh, Dalton Trans. 46 (2017) 13065–13076.
[10] H. Aneetha, M.J. Tenorio, M.C. Puerta, P. Valerga, J. Organomet. Chem. 663 (2002) 151–157.
[11] O. Navarro, S.P. Nolan, Synthesis 2 (2006) 366–367.
[12] G.M. Sheldrick, SADABS, Program for Empirical Absorption Correction of Area Detector Data, University of Göttingen, Germany, 2002.
[13] G.M. Sheldrick, SHELXL-2014, Program for Crystal Structure Refinement, University of Göttingen, Göttingen, Germany, 2014.