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Synthesis and catalytic activity of *N*-heterocyclic carbene silver complexes derived from 1-[2-(pyrazol-1-yl)phenyl]imidazole

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ABSTRACT

Six mono- and dinuclear *N*-heterocyclic carbene (NHC) silver complexes based on 1-[2-(pyrazol-1-yl) phenyl]imidazole have been synthesized and characterized by elemental analysis and NMR spectroscopy, and their structures have been confirmed by single crystal X-ray diffraction. The *N*-functionalized carbene ligands exhibit versatile coordination modes in these silver complexes. *N*-[2-(3,5-Dimethylpyrazol-1-yl)phenyl]-*N*-benzylimidazol-2-ylidene (L) acts as a monodentate ligand through the carbene carbon in mononuclear LAgCl. While in dinuclear $L_2Ag_2(PF_6)_2$ and $L'_2Ag_2(PF_6)_2$ (L′ = *N*-[2-(pyrazol-1-yl)phenyl]-*N*-benzylimidazol-2-ylidene), L and L′ act as bridging bidentate ligands through the pyrazolyl nitrogen and the carbene carbon atoms to two silver atoms. Though, these two silver atoms have different coordination environments. In the former, one silver atom coordinates with two carbene carbons, the other coordinates with two pyrazolyl nitrogen atoms. In the latter, each silver atom coordinates with one carbene carbon and one pyrazolyl nitrogen atom, respectively. A dinuclear macrocyclic structure is observed in *m*-xylyl bridging tetradentate bis-NHC complexes $L_2Ag_2(BF_4)_2$ and $(L)CH_2C_6H_4CH_2(L)Ag_2(BF_4)_2$, in which the coordination mode of carbene ligands is similar with that in $L_2Ag_2(PF_6)_2$. Preliminary catalytic tests show that all these complexes exhibit highly effective catalytic activity in the three-component coupling reaction of alkyne, aldehyde and amine forming propargylamines.

1. Introduction

Transition metal complexes of *N*-heterocyclic carbenes (NHCs) have been the subject of extensive investigations because of their successful applications in coordination chemistry and homogeneous and asymmetric catalyses [1–4]. Among these complexes, NHC silver complexes have received special attention due to their structural diversity, wide application as effective carbene transfer agents [5–7] and prominent biological activity [8–12]. However, despite the fact that silver complexes have been extensively used to catalyze the formation of C–C and C–E (E = heteroatom) bonds [13–15], the utility of NHC silver complexes in chemical catalysis remains scarcely explored, and only a few examples were reported. Representative successes have demonstrated that NHC silver complexes exhibit good catalytic activities for diboration of alkenes [16], carbomagnesiation of terminal alkenes [17], direct alkynylation of isatins [18], CO_2 fixation [19], cyanosilylation of imines [20], and ring-opening polymerization of L-lactide [21–23]. Recently, NHC silver complexes have also been successfully used to catalyze the three-component coupling reaction of aldehyde, alkyne and amine to propargylamines [24–26]. With the aforementioned progress as inspirations, the exploitation of wider applications of NHC silver complexes in catalyzed organic transformations is aspired, in view of the high catalytic activity of silver compounds in many organic reactions [13–15] and the ease of preparation of NHC silver complexes. In this paper, we report the synthesis of six NHC silver complexes based on 1-[2-(pyrazol-1-yl) phenyl]imidazole, and their catalytic activity in the three-component coupling reaction of alkyne, aldehyde and amine forming propargylamines.

2. Results and discussion

2.1. Synthesis of N-[2-(pyrazol-1-yl)phenyl]-N-benzylimidazol-2-ylidene silver complexes

1-[2-(Pyrazol-1-yl)phenyl]imidazoles (**3**) and (**4**) were synthesized by the copper catalyzed coupling reaction of 1-(2-iodophenyl) pyrazoles (**1**) and (**2**) with imidazole (Scheme 1). Treatment of these two substituted imidazoles with benzyl chloride gave the imidazolium salts (**5**) and (**6**). The hexafluorophosphate and

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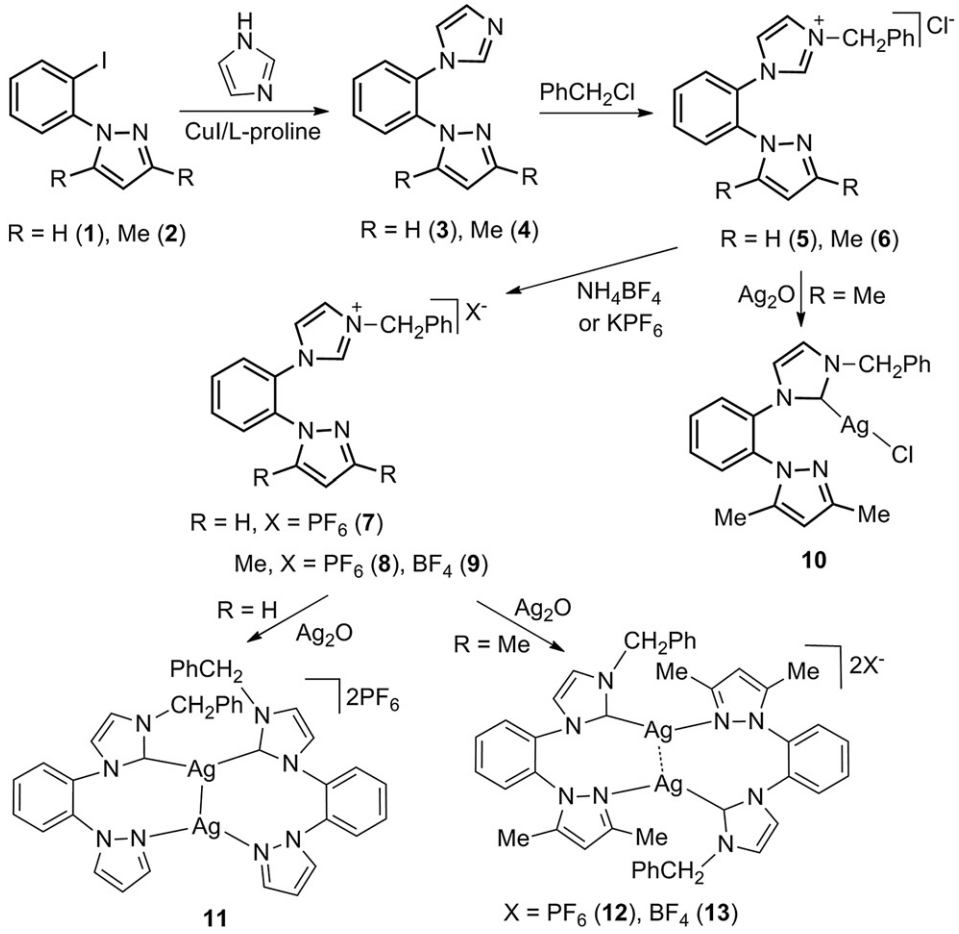


Scheme 1.

tetrafluoroborate salts (**7**–**9**) were obtained by the anion exchange reaction of (**5**) and (**6**) with KPF_6 or NH_4BF_4, respectively. Reaction of these imidazolium salts with Ag_2O gave the carbene complexes (**10**–**13**) in good yields. Complexes **10**–**13** have been characterized by elemental analyses and NMR spectroscopy. Compared with the spectra of the imidazolium salts **5**–**9**, a notable change in the ^1H NMR spectra of **10**–**13** was the disappearance of the characteristic proton signal of imidazolium, indicating the formation of NHC silver complexes along with the deprotonation of the acidic hydrogen. At the same time, an obvious carbene carbon signal was observed at *ca.* 179 ppm in the ^{13}C NMR spectra of **11**–**13**. In the meanwhile, neither the signal of the carbene carbon in **10** nor the silver–carbon coupling in **11**–**13** was observed, which may be attributed to the fluxional behavior of these NHC complexes in solution [27,28].

The molecular structures of **10**–**13** have been further confirmed by X-ray structural analyses, and are presented in Figs. 1–4, respectively. It seems that the coordination environment of silver atoms in these complexes markedly depends on the substituents of pyrazolyl rings and the anions. Fig. 1 shows that complex **10** has a monomeric structure with a two-coordinate silver atom. *N*-[2-(3,5-Dimethylpyrazol-1-yl)phenyl]-*N*-benzylimidazol-2-ylidene acts a monodentate ligand by the carbene carbon atom, and the pyrazolyl nitrogen atom does not take part in the coordination to the silver center. The coordination geometry around the silver atom is nearly linear. The angle of C(14)–Ag(1)–Cl(1) is 171.55(5)°, falling within the range of values observed in other analogous monomeric two-coordinate (NHC)AgX complexes (166–176°) [5,25]. The Ag–$C_{carbene}$ and Ag–Cl bond distances are 2.075(2) and 2.3228(8) Å, respectively, comparable to those in sterically demanding NHC supported silver chlorides, such as (IDD)AgCl (Ag–$C_{carbene}$ 2.067(4) and Ag–Cl 2.3200(9) Å, IDD = 1,3-bis(dodecyl)imidazol-2-ylidene) [29], (IBp)AgCl (Ag–$C_{carbene}$ 2.079(2) and Ag–Cl 2.3440(11) Å, IBp = 1,3-bis(2-phenylphenyl)imidazol-2-ylidene) [30] and (IPr*)AgCl (Ag–$C_{carbene}$ 2.081(2) and Ag–Cl 2.3189(9) Å, IPr* = 1,3-

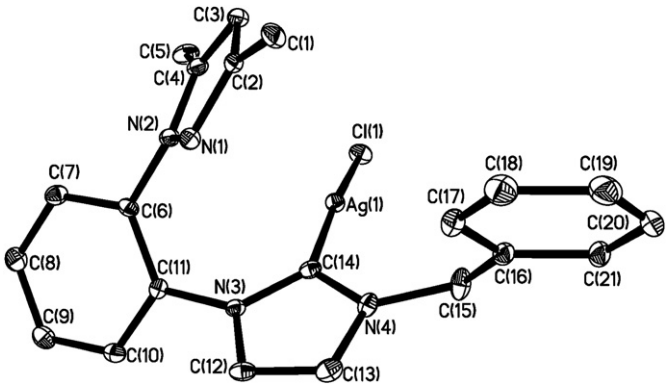


Fig. 1. The molecular structure of **10**. The thermal ellipsoids are drawn at the 30% probability level. Selected bond distances (Å) and angles (°): Ag(1)–C(14), 2.075(2), Ag(1)–Cl(1) 2.3228(8), C(12)–C(13) 1.344(3), N(3)–C(14) 1.356(2) Å; C(14)–Ag(1)–Cl(1) 171.55(5), N(4)–C(15)–C(16) 114.3(2), N(3)–C(14)–N(4) 104.1(2), C(11)–N(3)–C(14) 125.2(2)°.

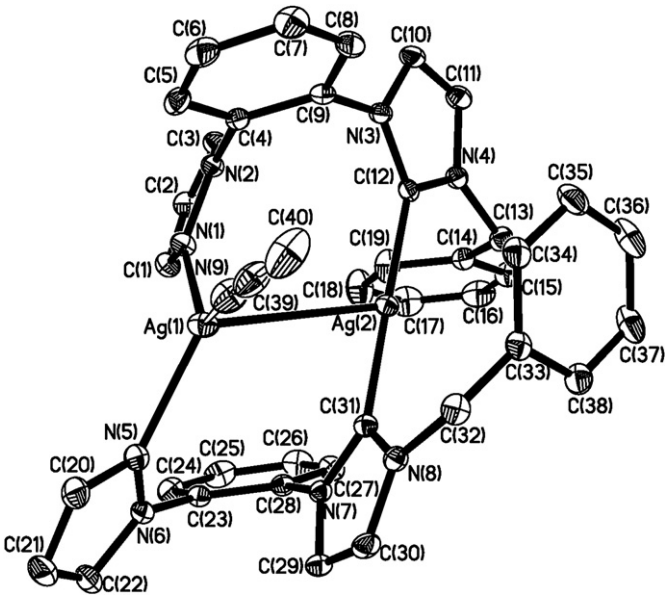


Fig. 2. The molecular structure of **11**.CH_3CN. The thermal ellipsoids are drawn at the 30% probability level. The PF_6^- anions have been deleted for clarity. Selected bond distances (Å) and angles (°): Ag(1)–N(1) 2.227(5), Ag(1)–N(5) 2.276(5), Ag(1)–N(9) 2.225(7), Ag(1)–Ag(2) 3.0667(8), Ag(2)–C(12) 2.091(5), Ag(2)–C(31) 2.088(5) Å; N(1)–Ag(1)–N(5) 115.5(2), C(12)–Ag(2)–C(31) 178.8(2), N(3)–C(12)–N(4) 104.1(4), N(7)–C(31)–N(8) 103.6(4), N(4)–C(13)–C(14) 112.9(5), N(8)–C(32)–C(33) 113.9(4), C(9)–N(3)–C(12) 123.8(4), C(28)–N(7)–C(31) 123.2(4)°.

bis(2,6-bis(diphenylmethyl)-4-methylphenyl)imidazol-2-ylidene) [31]. These data suggest that *N*-[2-(3,5-dimethylpyrazol-1-yl) phenyl]-*N*-benzylimidazol-2-ylidene is a considerably sterically demanding ligand possibly owing to the rigidity of three aromatic rings.

Figs. 2 and 3 illustrate that the NHC ligands in **11** and **12** act as bridging bidentate ligands through the pyrazolyl nitrogen and the carbene carbon atoms to two silver atoms. Though, these two NHC

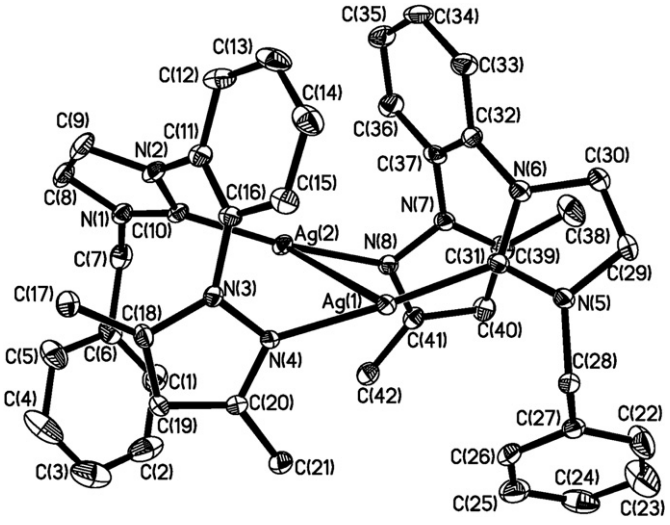


Fig. 3. The molecular structure of **12**. The thermal ellipsoids are drawn at the 30% probability level. The PF_6^- anions have been deleted for clarity. Selected bond distances (Å) and angles (°): Ag(1)–C(31) 2.086(3), Ag(1)–N(4) 2.119(3), Ag(1)–Ag(2) 3.269(1), Ag(2)–C(10) 2.080(4), Ag(2)–N(8) 2.126(3) Å; C(31)–Ag(1)–N(4) 174.6(1), C(10)–Ag(2)–N(8) 173.7(1), N(5)–C(31)–N(6) 105.3(3), N(1)–C(10)–N(2) 104.5(3), N(1)–C(7)–C(6) 110.7(3), N(5)–C(28)–C(27) 111.1(3), C(10)–N(2)–C(11) 123.6(3), C(31)–N(6)–C(32) 124.9(3)°.

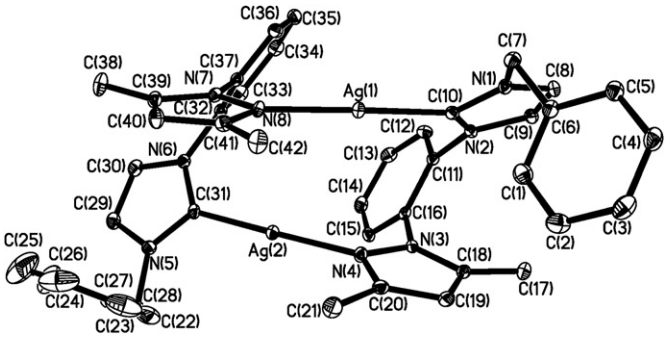


Fig. 4. The molecular structure of **13**. The thermal ellipsoids are drawn at the 30% probability level. The uncoordinated solvent and BF_4^- anions have been deleted for clarity. Selected bond distances (Å) and angles (°): Ag(1)–C(10) 2.077(2), Ag(1)–N(8) 2.131(2), Ag(2)–C(31) 2.063(2), Ag(2)–N(4) 2.104(2), Ag(1)…Ag(2) 3.461(1) Å; C(10)–Ag(1)–N(8) 176.66(7), C(31)–Ag(2)–N(4) 174.3(4), N(1)–C(7)–C(6) 111.3(2), N(5)–C(28)–C(27) 109.9(2), N(1)–C(10)–N(2) 103.8(2), N(5)–C(31)–N(6) 104.1(2)°.

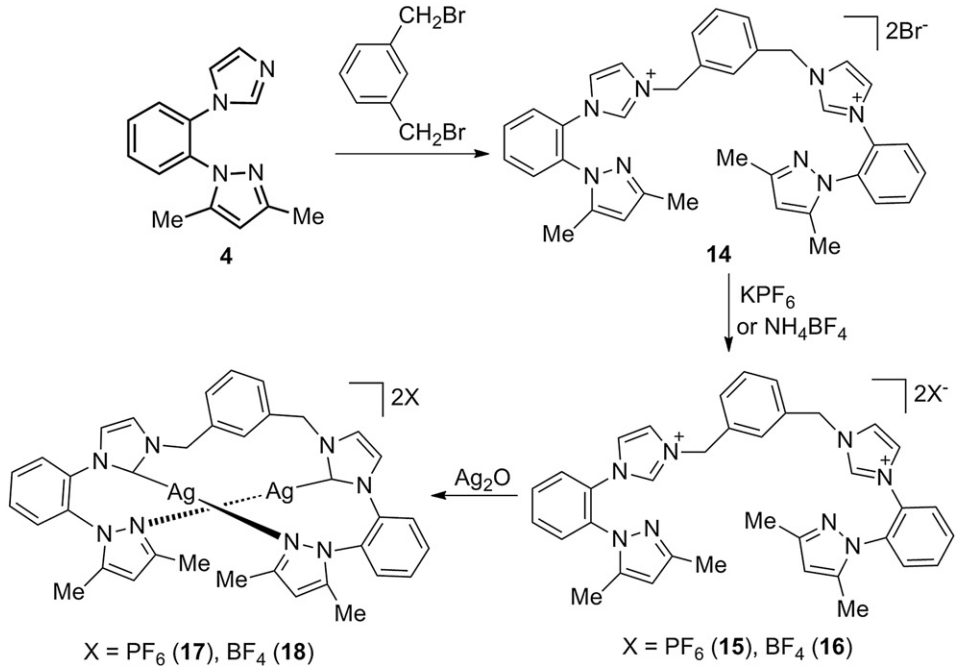
ligands exhibit different coordination modes in these two complexes. In **11**, two NHCs show a head (carbene)–to head (carbene) and a tail (nitrogen)–to tail (nitrogen) coordination modes to two silver atoms, respectively. While in **12**, the NHCs only show a head–to tail coordination mode to two silver atoms. Obviously, the substituents of pyrazolyl rings significantly affect the coordination modes of the NHC ligands in **11** and **12**. The Ag–$C_{carbene}$ and Ag–$N_{pyrazolyl}$ bond distances are similar in these two complexes, but the Ag–Ag distance (3.0667(8) Å) in **11** is considerably shorter than that in **12** (3.269(3) Å). These values are shorter than the sum of the van der Waals radii for silver (3.44) Å [32], suggesting significant silver–silver bonding in these two complexes.

Fig. 4 clarifies that the fundamental fragment of **13** is similar with that in **12**. However, the long Ag–Ag separation (3.461(1) Å) in **13** suggests that the silver–silver interaction is very weak in this complex. The C(10)–Ag(1)–N(8) angle is 176.66(7)°, slightly larger than the C(31)–Ag(2)–N(4) angle of 174.3(4)° and the corresponding C–Ag–N angles (174.6(1) and 173.7(1)° in **12**. The other notable difference between **13** and **12** is the dihedral angles between the phenyl plane and the pyrazolyl ring, or the imidazolyl ring. For example, the dihedral angles of the C(11)–C(16) phenyl plane with the N(3)–C(18) pyrazolyl ring and the N(1)–C(8) imidazolyl ring in **13** are 62.4° and 59.1°, respectively. While the corresponding dihedral angles in **12** are 68.6° (the C(11)–C(16) phenyl plane with the N(3)–C(18) pyrazolyl ring) and 119.3° (the C(11)–C(16) phenyl plane with the N(1)–C(8) imidazolyl ring). These data reflect the different degree of distortion in these two complexes.

2.2. Synthesis of *m*-xylyl bridging bis-NHC silver complexes

Transition metal complexes with bis- or tris-NHC ligands have shown higher stability and enhanced catalytic activities compared with those with monodentate NHC ligands, which drives the rapid development of polydentate NHCs [33–36]. Xylyl-linked bis-NHC ligands have been extensively investigated in recent years [37–43], and they usually acted as bidentate ligands in complexes. However, polydentate xylyl-linked bis-NHCs are rare. Herein, upon treatment of bis(imidazolium) salts **15** and **16** with Ag_2O, two tetradentate bis-NHC complexes **17** and **18** were obtained (Scheme 2).

Complexes **17** and **18** have also been characterized by elemental analyses and NMR spectroscopy. The ^1H NMR spectra of these two complexes indicated the methylene protons of the *m*-xylyl group were not equivalent, and an AB system was observed at room temperature. This suggests that the macrocyclic structures of these



Scheme 2.

two complexes are reserved in solution, which prevents the free rotation of the NHC ligand. The molecular structure of **18** has been confirmed by X-ray crystallography and is presented in Fig. 5. As shown in Fig. 5, the NHC acts as a tetradentate ligand through two carbene carbons and two pyrazolyl nitrogen atoms to two silver centers, leading to the formation of twisted dinuclear macrocyclic structures. Each silver atom coordinates with one carbene carbon and one pyrazolyl nitrogen. The coordination mode of the NHC ligand is similar with that in **12**. The key geometric parameters, such as the Ag–C and Ag–N bond distances, the C–Ag–N angles, are also similar to those in **12**. The Ag–Ag distance is 3.3834(8) Å, slightly shorter than the sum of the van der Waals radii for silver [32], suggesting a weak silver–silver interaction. The dihedral angles of the C(6)–C(11) phenyl plane with the N(1)–C(2) pyrazolyl ring (108.3°) and the N(3)–C(14) imidazolyl ring (117.2°) as well as the C(26)–C(31) phenyl plane with the N(7)–C(33) pyrazolyl ring (112.0°) and the N(5)–C(23) imidazolyl ring (116.7°) reveal considerable distortion between the phenyl plane with the pyrazolyl and the imidazolyl rings, respectively. It is noted that the N(4)–C(15)–C(16) angle of 115.4(3)° deviates from the tetrahedral geometry of the sp^3-hybridized carbon, suggesting a large steric repulsion in this complex.

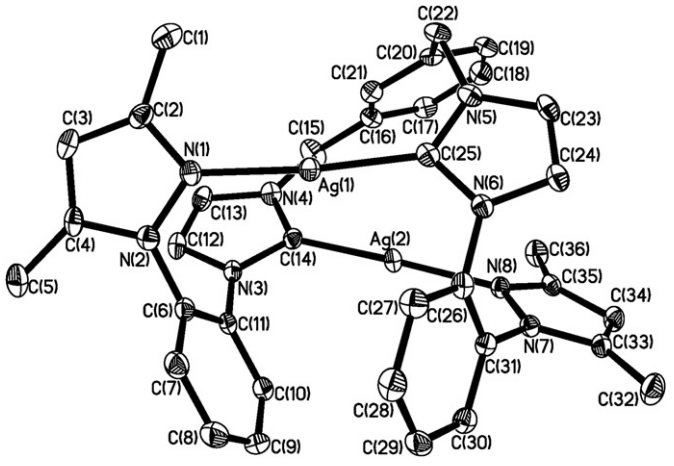
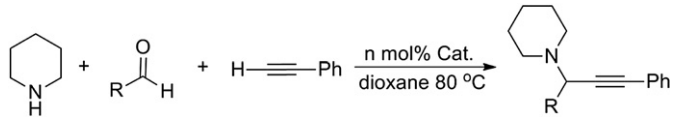


Fig. 5. The molecular structure of **18**. The thermal ellipsoids are drawn at the 30% probability level. The uncoordinated solvents and BF_4^- anions have been deleted for clarity. Selected bond distances (Å) and angles (°): Ag(1)–C(25) 2.078(4), Ag(1)–N(1) 2.122(3), Ag(2)–C(14) 2.062(3), Ag(2)–N(8) 2.106(3), Ag(1)…Ag(2) 3.3834(8) A; C(25)–Ag(1)–N(1) 173.9(1), C(14)–Ag(2)–N(8) 175.1(1), N(4)–C(15)–C(16) 115.4(3), N(5)–C(22)–C(20) 109.2(3), N(4)–C(14)–N(3) 103.6(3), N(5)–C(25)–N(6) 103.9(3)°.

2.3. Catalytic activity of the NHC silver complexes

The three-component coupling reaction of alkyne, aldehyde and amine to propargylamines catalyzed by transition metals has attracted considerable attention in recent years [44], due to the wide applications of propargylamines as key intermediates in the construction of nitrogen-containing biologically active compounds. Although silver compounds exhibited highly effective catalytic activity for this three-component coupling reaction [45], only several NHC–Ag systems were exploited as catalysts [24–26], and most of them were mononuclear silver complexes. Furthermore, it seems that the monomeric (NHC)AgX complexes showed higher catalytic activity than the dimeric $[(NHC)AgX]_2$ and the cationic biscarbene silver complexes [25]. Herein, our preliminary studies showed that all these monomeric complex **10** and dinuclear cationic complexes **11**–**13** as well as **17** and **18** exhibited effective catalytic activity in the three-component coupling reaction of phenylacetylene, aldehyde and piperidine (Table 1). Moderate yields were obtained when 3 mol% of **10** was used as the catalyst for the coupling reaction of *para*-formaldehyde (Table 1, entry 1). Unfortunately, this complex showed low catalytic activity for the coupling of benzaldehyde (entry 2). However, high catalytic activity for the coupling of cyclohexanecarboxaldehyde was observed (entry 4). It is interesting that the catalytic activity of dinuclear complexes **11**–**13** as well as **17** and **18** is almost two times that of mononuclear complex **10** (entries 5–9), indicating that two silver atoms in dinuclear complexes simultaneously play the catalytic

Table 1
Catalytic activity of the NHC silver complexes.



Entry	R	Cat.	n	*t*/h	Yield (%)[a,b]
1	H	**10**	3	2	55
2	Ph	**10**	3	12	13
3	Cyclohexyl	**10**	2	8	50
4	Cyclohexyl	**10**	3	8	95
5	Cyclohexyl	**11**	1.5	8	94
6	Cyclohexyl	**12**	1.5	8	97
7	Cyclohexyl	**13**	1.5	8	97
8	Cyclohexyl	**17**	1.5	2	93
9	Cyclohexyl	**18**	1.5	8	94

[a] Isolated yield.
[b] Average of two runs.

role. When complex **17** was used the catalyst, the coupling reaction proceeded significantly faster (entry 8). In addition, the different coordination mode of NHC has little effect on the catalytic activity of complexes (entries 5 and 6).

In summary, six NHC silver complexes derived from 1-[2-(pyrazol-1-yl)phenyl]imidazole have been synthesized. The *N*-functionalized NHC ligands exhibit versatile coordination modes in these silver complexes. For example, the NHC acts as a monodentate ligand in mononuclear complex **10**. While a head (carbene)–to head (carbene) or head (carbene)–to tail (nitrogen) coordination mode is found in dinuclear complexes **11** and **12**, respectively. In addition, *m*-xylyl bridging tetradentate bis-NHCs are observed in complexes **17** and **18**. Preliminary catalytic studies prove that all these mononuclear and dinuclear complexes exhibit good catalytic activity in the three-component coupling reaction of alkyne, aldehyde and amine to propargylamines. Studies on expanding the scope of substrates, the structural modification of NHC and the structure-activity relationship of catalysts are ongoing in our laboratory.

3. Experimental

NMR (^{1}H and ^{13}C) were recorded on a Bruker 400 spectrometer using $CDCl_3$ as solvent unless otherwise noted, and the chemical shifts were reported in ppm with respect to the reference (internal $SiMe_4$ for ^{1}H and ^{13}C NMR spectra). Element analyses were carried out on an Elementar Vairo EL analyzer. HR mass spectra were obtained on a Varian QFT-ESI spectrometer. Melting points were measured with an X-4 digital micro melting-point apparatus and were uncorrected. 2-Iodophenylhydrazine [46] was prepared according to the literature method.

3.1. Synthesis of 1-(2-iodophenyl)pyrazole (*1*)

Concentrated hydrochloric acid (14.5 ml, 87 mmol) was added dropwise to the stirred mixture of 2-iodophenylhydrazine (14 g, 60 mmol) and malondialdehyde bis(dimethyl acetal) (12 g, 72 mmol) at 0 °C. After the addition completed, the reaction mixture was stirred for 2 h at room temperature, and water (20 ml) was added. Then, the reaction mixture was neutralized with NaOH solution (1 M). The solution was extracted with ethyl acetate (3 × 30 ml). The organic phases were combined, and dried over anhydrous $MgSO_4$. After the solvent was removed under reduced pressure, red oil was obtained. Yield: 11.8 g (73%). ^{1}H NMR: δ 6.49 (t, J = 2.1 Hz, 1H, H^4 of pyrazole), 7.16 (dt, J = 2.0 Hz, J = 7.9 Hz, 1H), 7.41–7.48 (m, 2H), 7.98 (dd, J = 0.9 Hz, J = 8.0 Hz, 1H) (C_6H_4), 7.73 (d, J = 2.3 Hz, 1H), 7.77 (d, J = 1.4 Hz, 1H) (H^3 and H^5 of pyrazole) ppm. ^{13}C NMR: δ 94.4, 106.6, 128.2, 129.0, 130.2, 131.1, 140.1, 140.8, 143.4 (C_6H_4 and carbons of pyrazole) ppm. HRMS–ESI (*m*/*z*): 292.9547 (Calc. for $C_9H_7IN_2Na$: 292.9552, $[M + Na]^+$, 100%).

3.2. Synthesis of 1-(2-iodophenyl)-3,5-dimethylpyrazole (*2*)

Acetylacetone (6.03 g, 60.3 mmol) was slowly added to the solution of 2-iodophenylhydrazine (12.8 g, 54.7 mmol) in ethanol (100 ml). The mixture was stirred and heated at reflux for 8 h. After cooling to room temperature, the solvent was removed under reduced pressure. The residue was dissolved in water (100 ml), and extracted with ethyl ether (3 × 40 ml). The organic phases were combined, washed with saturated $NaHCO_3$ solution (3 × 30 ml), and dried over anhydrous $MgSO_4$. After the solvent was removed under reduced pressure, red oil was obtained. Yield: 13.1 g (80%). ^{1}H NMR: δ 2.12, 2.33 (s, s, 3H, 3H, CH_3), 6.01 (s, 1H, H^4 of pyrazole), 7.17 (td, J = 7.7 Hz, J = 1.5 Hz, 1H) 7.36 (dd, J = 7.8 Hz, J = 1.5 Hz, 1H), 7.46 (dd, J = 11.1 Hz, J = 4.0 Hz, 1H), 7.95 (d, J = 7.9 Hz, 1H) (C_6H_4) ppm. ^{13}C NMR: δ 11.7, 13.7 (CH_3), 98.2, 105.6, 129.0, 129.4, 130.6, 139.5, 140.4, 142.6, 149.0 (C_6H_4 and carbons of pyrazole) ppm. HRMS–ESI (*m*/*z*): 320.9858 (Calc. for $C_{11}H_{11}IN_2Na$: 320.9865, $[M + Na]^+$, 100%).

3.3. Synthesis of 1-[2-(pyrazol-1-yl)phenyl]imidazole (*3*)

Compound **1** (2.7 g, 10 mmol), imidazole (0.82 g, 12 mmol), K_2CO_3 (2.76 g, 20 mmol), L-proline (0.23 g, 2 mmol) and CuI (0.19 g, 1 mmol) were added to DMSO (10 ml) under Ar atmosphere. The mixture was stirred and heated at 90 °C for 48 h. After cooling to room temperature, saturated NaCl solution (30 ml) was added. The aqueous solution was extracted with ethyl acetate (3 × 30 ml). The organic phases were combined and washed again with saturated NaCl solution (3 × 30 ml), and then dried over anhydrous Na_2SO_4. After the solvent was removed under reduced pressure, the residue was purified by column chromatography on silica using ethyl acetate/hexane (1/1 v/v) as the eluent. The yellow eluate was concentrated to dryness to give slightly yellow oil of **3**. Yield: 1.15 g (55%). ^{1}H NMR: δ 6.34 (t, J = 2.0 Hz, 1H, H^4 of pyrazole), 6.85 (s, 1H), 7.03 (d, J = 2.4 Hz, 1H), 7.42 (s, 1H), 7.13 (s, 1H), 7.42–7.60 (m, 3H), 7.71 (s, 1H), 7.76 (dd, J = 1.4 Hz, J = 7.8 Hz, 1H) (protons of imidazole, pyrazole and phenyl) ppm. ^{13}C NMR: δ 108.0, 119.8, 126.7, 127.3, 129.0, 129.4, 129.9, 130.2, 130.3, 131.4, 136.9, 141.4 (C_6H_4, carbons of imidazole and pyrazole) ppm. HRMS–ESI (*m*/*z*): 233.0792 (Calc. for $C_{12}H_{10}N_4Na$: 233.0803, $[M + Na]^+$, 100%).

3.4. Synthesis of 1-[2-(3,5-dimethylpyrazol-1-yl)phenyl]imidazole (*4*)

This compound was obtained similarly using **2** instead of **1** as described above for **3** as slightly yellow solids. Yield: 74%, mp 80–82 °C. ^{1}H NMR: δ 1.70, 2.28 (s, s, 3H, 3H, CH_3), 5.87 (s, 1H, H^4 of pyrazole), 6.78 (s, 1H), 7.05 (s, 1H), 7.33 (s, 1H) (protons of imidazole), 7.42–7.60 (m, 4H, C_6H_4) ppm. ^{13}C NMR: δ 10.4, 13.5 (CH_3), 106.3 (C^4 of pyrazole), 118.9, 124.8, 128.4, 130.0, 130.1, 130.2, 133.2, 134.3, 136.5, 141.8, 150.0 (C_6H_4, carbons of imidazole and pyrazole) ppm. Anal. Calc. for $C_{14}H_{14}N_4$: C, 70.57; H, 5.92; N, 23.51. Found: C, 70.37; H, 5.92; N, 23.49%.

3.5. Synthesis of L′HCl (*5*) (L′ = *N*-[2-(pyrazol-1-yl)phenyl]-*N*-benzylimidazol-2-ylidene)

The mixture of **3** (0.21 g, 1 mmol) and $PhCH_2Cl$ (0.12 ml, 1 mmol) in CH_3CN (2 ml) was stirred and heated at reflux for 24 h. After

cooling to room temperature, the solvent was removed under reduced pressure, the residue was washed with anhydrous ethyl ether, and dried *in vacuo* to give viscous oils of **5**. Yield: 0.32 g (94%). ^{1}H NMR: δ 5.74 (s, 2H, CH_2), 6.37 (s, br, 1H, H^4 of pyrazole), 6.98 (s, 1H), 7.36–7.40 (m, 4H), 7.54–7.59 (m, 5H), 7.63–7.68 (m, 1H), 7.74 (s, 1H), 7.82 (d, J = 7.2 Hz, 1H) (C$_6H_4$, C$_6H_5$, protons of imidazole and pyrazole), 10.61 (s, 1H, proton of imidazolium) ppm. ^{13}C NMR: δ 53.4 (*C*H$_2$), 108.3 (*C*^{4} of pyrazole), 122.1, 122.9, 126.8, 127.6, 129.3 (3 C), 129.4, 129.9, 131.2, 131.9, 133.3, 135.2, 138.3, 142.1 (*C*$_6$H$_4$, carbons of imidazole and pyrazole) ppm. HRMS–ESI (m/z): 301.1446 (Calc. for $C_{19}H_{17}N_4^+$: 301.1448, [M − Cl]$^+$, 100%).

3.6. Synthesis of LHCl (**6**) (L = N-[2-(3,5-dimethylpyrazol-1-yl) phenyl]-N-benzylimidazol-2-ylidene)

The mixture of **4** (0.24 g, 1 mmol) and PhCH$_2$Cl (0.12 ml, 1 mmol) in CH$_3$CN (2 ml) was stirred and heated at reflux for 24 h. After cooling to room temperature, ethyl acetate (10 ml) was added. White solids were formed, which were filtered and washed with dried ethyl ether to give white solids of **6**. Yield: 0.33 g (90%), mp 94–96 °C. ^{1}H NMR: δ 2.03, 2.06 (s, s, 3H, 3H, C*H*$_3$), 5.78 (s, 2H, C*H*$_2$), 5.90 (s, 1H, H^4 of pyrazole), 6.92 (s, 1H), 7.34–7.40 (m, 3H), 7.49–7.53 (m, 4H), 7.65–7.69 (m, 2H), 7.98–8.01 (m, 1H) (C$_6H_4$, C$_6H_5$ and protons of imidazole), 10.78 (s, 1H, proton of imidazolium) ppm. ^{13}C NMR: δ 11.4, 13.3 (*C*H$_3$), 53.5 (*C*H$_2$), 107.1 (*C*^{4} of pyrazole), 122.1, 122.4, 126.7, 129.1, 129.3, 129.4, 129.5, 131.0, 131.4, 131.5, 133.2, 133.6, 137.7, 141.6, 150.7 (*C*$_6$H$_4$, *C*$_6$H$_5$, carbons of imidazole and pyrazole) ppm. Anal. Calc. for $C_{21}H_{21}ClN_4$: C, 69.13; H, 5.80; N, 15.36. Found: C, 69.43; H, 5.98; N, 15.24%.

3.7. Synthesis of L′HPF$_6$ (**7**)

Compound **5** (0.17 g, 0.5 mmol) was added to the solution of KPF$_6$ (0.11 g, 0.6 mmol) in H$_2$O (30 ml). The mixture was stirred for 30 min at room temperature, a white precipitate was formed. The reaction mixture was extracted with CH$_2$Cl$_2$ (3 × 10 ml), the organic phases were combined and dried over anhydrous MgSO$_4$. After removing the solvent, the residue was washed with ethyl ether to give a white and strongly hygroscopic solid of **7**. Yield: 0.17 g (77%). ^{1}H NMR: δ 5.28 (s, 2H, C*H*$_2$), 6.33 (t, J = 2.2 Hz, 1H, H^4 of pyrazole), 7.04 (t, J = 1.7 Hz, 1H), 7.22–7.24 (m, 1H), 7.33–7.35 (m, 3H), 7.38–7.40 (m, 3H), 7.50–7.52 (m, 2H), 7.61–7.65 (m, 3H) (C$_6H_4$, C$_6H_5$ and protons of imidazole), 8.37 (s, 1H, proton of imidazolium) ppm. ^{13}C NMR: δ 53.6 (*C*H$_2$), 108.3 (*C*^{4} of pyrazole), 122.2, 123.6, 126.5, 127.4, 128.8, 129.0, 129.5, 129.7, 129.8, 131.1, 132.1, 132.4, 135.2, 136.2, 142.2 (*C*$_6$H$_4$, *C*$_6$H$_5$, carbons of imidazole and pyrazole) ppm. Anal. Calc. for $C_{19}H_{17}F_6N_4P$: C, 51.13; H, 3.84; N, 12.55. Found: C, 51.41; H, 3.68; N, 12.22%.

3.8. Synthesis of LHPF$_6$ (**8**)

This compound was obtained similarly using **6** instead of **5** as described above for **7** as white solids. Yield: 75%, mp 116–118 °C. ^{1}H NMR: δ 2.03, 2.06 (s, s, 3H, 3H, C*H*$_3$), 5.36 (s, 2H, C*H*$_2$), 5.91 (s, 1H, H^4 of pyrazole), 7.10 (s, 1H), 7.28 (s, 1H), 7.34–7.36 (m, 2H), 7.42–7.44 (m, 3H), 7.50 (d, J = 7.5 Hz, 1H), 7.63–7.71 (m, 2H), 7.77 (d, J = 7.1 Hz, 1H) (C$_6H_4$, C$_6H_5$ and protons of imidazole), 8.40 (s, 1H, proton of imidazolium) ppm. ^{13}C NMR: δ 11.1, 13.3 (*C*H$_3$), 53.9 (*C*H$_2$), 107.2 (*C*^{4} of pyrazole), 122.4, 123.2, 126.7, 129.1, 129.2, 129.6, 129.8, 130.9, 131.3, 131.7, 132.2, 133.8, 135.5, 141.7, 150.8 (*C*$_6$H$_4$, *C*$_6$H$_5$, carbons of imidazole and pyrazole) ppm. Anal. Calc. for $C_{21}H_{21}F_6N_4P$: C, 53.17; H, 4.46; N, 11.81. Found: C, 53.13; H, 4.51; N, 11.74%.

3.9. Synthesis of LHBF$_4$ (**9**)

This compound was obtained similarly using NH$_4$BF$_4$ instead of KPF$_6$ as described above for **7** as white solids. Yield: 77%, mp 130–132 °C. ^{1}H NMR: δ 2.00, 2.01 (s, s, 3H, 3H, C*H*$_3$), 5.39 (s, 2H, C*H*$_2$), 5.87 (s, 1H, H^4 of pyrazole), 7.03 (t, J = 1.8 Hz, 1H), 7.35–7.38 (m, 6H), 7.46–7.49 (m, 1H), 7.61–7.66 (m, 2H), 7.78–7.81 (m, 1H) (C$_6H_4$, C$_6H_5$ and protons of imidazole), 8.68 (s, 1H, proton of imidazolium) ppm. ^{13}C NMR: δ 11.1, 13.3 (*C*H$_3$), 53.7 (*C*H$_2$), 107.1 (*C*^{4} of pyrazole), 122.4, 123.0, 126.7, 129.1, 129.2, 129.5, 129.6, 130.9, 131.4, 131.5, 132.7, 133.8, 135.9, 141.6, 150.7 (*C*$_6$H$_4$, *C*$_6$H$_5$, carbons of imidazole and pyrazole) ppm. Anal. Calc. for $C_{21}H_{21}BF_4N_4$: C, 60.60; H, 5.09; N, 13.46. Found: C, 60.43; H, 5.09; N, 13.52%.

3.10. Synthesis of LAgCl (**10**)

The mixture of **6** (0.33 g, 0.9 mmol) and Ag$_2$O (0.14 g, 0.6 mmol) in CH$_2$Cl$_2$ (10 ml) was stirred at room temperature for 24 h in the absence of light. The solution was filtered and concentrated to dryness. A red solid was obtained. Yield: 0.42 g (99%), mp 69–71 °C. ^{1}H NMR: δ 1.93, 2.17 (s, s, 3H, 3H, C*H*$_3$), 5.31 (s, 2H, C*H*$_2$), 5.84 (s, 1H, H^4 of pyrazole), 6.88 (s, 2H), 7.17–7.19 (m, 2H), 7.36–7.38 (m, 3H), 7.50–7.53 (m, 1H), 7.59–7.62 (m, 1H), 7.70–7.73 (m, 1H) (C$_6H_4$, C$_6H_5$ and protons of imidazole) ppm. ^{13}C NMR: δ 9.9, 11.6 (*C*H$_3$), 54.1 (*C*H$_2$), 104.4 (*C*^{4} of pyrazole), 118.9, 121.7, 125.6, 125.7, 126.9, 127.3, 127.7, 128.4, 128.5, 133.1, 133.3, 134.6, 139.4, 148.1 (*C*$_6$H$_4$, *C*$_6$H$_5$, carbons of imidazole and pyrazole) ppm. The carbene carbon was not observed. Anal. Calc. for $C_{21}H_{20}AgClN_4$: C, 53.47; H, 4.27; N, 11.88. Found: C, 53.74; H, 4.04; N, 11.74%.

In addition, when heating **10** in dioxane at 80 °C for 1 h under Ar atmosphere, no obvious change was observed. After removing the solvent, the residue was monitored by ^{1}H NMR. The result indicated that the ^{1}H NMR spectrum of the residue was the same as that of **10**, suggesting that this complex was stable in the dioxane solution at 80 °C.

3.11. Synthesis of L′$_2$Ag$_2$(PF$_6$)$_2$ (**11**)

The mixture of **7** (0.17 g, 0.38 mmol) and Ag$_2$O (80 mg, 0.38 mmol) in CH$_2$Cl$_2$ (10 ml) was stirred at room temperature for 24 h in the absence of light. The solution was filtered and concentrated to *ca.* 2 ml, ethyl ether (5 ml) was added to give yellow solids of **11**. Yield: 0.38 g (91%), mp 153–155 °C. ^{1}H NMR (DMSO-d_6): δ 5.22 (s, 2H, C*H*$_2$), 6.43 (t, J = 2.2 Hz, 1H, H^4 of pyrazole), 7.07 (d, J = 6.4 Hz, 2H), 7.33–7.38 (m, 3H), 7.48 (s, 1H), 7.56–7.69 (m, 7H) (C$_6H_4$, C$_6H_5$ and protons of imidazole) ppm. ^{13}C NMR (DMSO-d_6): δ 52.9 (*C*H$_2$), 106.5 (*C*^{4} of pyrazole), 121.5, 123.1, 125.9, 126.1, 126.8, 127.1, 127.6, 129.0, 129.5, 131.3, 133.3, 134.3, 135.6, 141.0 (*C*$_6$H$_4$, *C*$_6$H$_5$, carbons of imidazole and pyrazole), 179.0 (*C*$_{Carbene}$) ppm. Anal. Calc. for $C_{38}H_{32}Ag_2F_{12}N_8P_2$: C, 41.25; H, 2.92; N, 10.13. Found: C, 41.44; H, 2.65; N, 10.21%.

3.12. Synthesis of L$_2$Ag$_2$(PF$_6$)$_2$ (**12**)

This compound was obtained similarly using **8** instead of **7** as described above for **11** as colorless solids. Yield: 90%, mp 116–118 °C. ^{1}H NMR (DMSO-d_6): δ 1.97, 2.05 (s, s, 3H, 3H, C*H*$_3$), 5.23 (s, 2H, C*H*$_2$), 6.19 (s, 1H, H^4 of pyrazole), 6.99 (s, br, 2H), 7.29–7.42 (m, 3H), 7.48 (s, 1H), 7.56–7.75 (m, 5H) (C$_6H_4$, C$_6H_5$ and protons of imidazole) ppm. ^{13}C NMR (DMSO-d_6): δ 11.2, 13.5 (*C*H$_3$), 53.9 (*C*H$_2$), 106.8 (*C*^{4} of pyrazole), 123.4, 123.6, 126.7, 127.9, 128.3, 128.7, 129.1, 131.0, 132.3, 132.8, 136.2, 136.6, 144.3, 150.6 (*C*$_6$H$_4$, *C*$_6$H$_5$, carbons of imidazole and pyrazole), 178.7 (*C*$_{Carbene}$) ppm. Anal. Calc. for $C_{42}H_{40}Ag_2F_{12}N_8P_2$: C, 43.39; H, 3.47; N, 9.64. Found: C, 43.33; H, 3.82; N, 9.65%.

3.13. Synthesis of $L_2Ag_2(BF_4)_2$ (**13**)

This compound was obtained similarly using **9** instead of **7** as described above for **11** as yellow solids. Yield: 86%, mp 114–117 °C. ^{1}H NMR (DMSO-d_6): δ 1.98, 2.08 (s, s, 3H, 3H, CH_3), 5.25 (s, 2H, CH_2), 6.23 (s, 1H, H^4 of pyrazole), 7.01 (s, br, 2H), 7.31–7.44 (m, 3H), 7.51 (s, 1H), 7.58–7.79 (m, 5H) (C_6H_4, C_6H_5 and protons of imidazole) ppm. ^{13}C NMR (DMSO-d_6): δ 11.3, 13.5 (CH_3), 54.0 (CH_2), 106.9 (C^4 of pyrazole), 123.4, 123.7, 126.8, 128.0, 128.4, 128.8, 129.1, 131.1, 132.4, 132.8, 136.3, 136.7, 144.4, 150.7 (C_6H_4, C_6H_5, carbons of imidazole and pyrazole), 178.6 ($C_{Carbene}$) ppm. Anal. Calc. for $C_{42}H_{40}Ag_2B_2F_8N_8$: C, 48.22; H, 3.85; N, 10.71. Found: C, 48.46; H, 4.07; N, 10.77%.

3.14. Synthesis of $(LH)CH_2C_6H_4CH_2(LH)Br_2$ (**14**)

The mixture of **4** (0.48 g, 2 mmol) and 1,3-bis(bromomethyl) benzene (0.26 g, 1 mmol) in CH_3CN (5 ml) was stirred and heated at reflux 24 h. After cooling to room temperature, the resulting solution was concentrated to *ca*. 2 ml. Ethyl acetate (10 ml) was added to give a slightly yellow and strongly hygroscopic solid of **14**. Yield: 0.62 g (84%). ^{1}H NMR: δ 2.02, 2.05 (s, s, 6H, 6H, CH_3), 5.76 (s, 4H, CH_2), 5.91 (s, 2H, H^4 of pyrazole), 6.78 (s, 1H), 7.18–7.21 (m, 1H), 7.48–7.50 (m, 2H), 7.64–7.71 (m, 6H), 7.99–8.02 (m, 2H), 8.28 (s, 2H), 8.49 (s, 1H) (C_6H_4, C_6H_5 and protons of imidazole), 10.57 (s, 2H, protons of imidazolium) ppm. ^{13}C NMR: δ 11.5, 13.4 (CH_3), 52.4 (CH_2), 107.3 (C^4 of pyrazole), 122.4, 123.6, 126.7, 129.5, 130.0, 130.1, 130.9, 131.3, 131.4, 131.5, 133.5, 134.4, 136.6, 141.4, 150.8 (C_6H_4, C_6H_5, carbons of imidazole and pyrazole) ppm. Anal. Calc. for $C_{36}H_{36}Br_2N_8$: C, 58.39; H, 4.90; N, 15.13. Found: C, 57.92; H, 4.48; N, 14.84%.

3.15. Synthesis of $(LH)CH_2C_6H_4CH_2(LH)(PF_6)_2$ (**15**)

KPF_6 (0.30 g, 1.6 mmol) was added to the solution of **14** (0.6 g, 0.8 mmol) in H_2O (20 ml). The reaction mixture was stirred for 10 min at room temperature. A white solid was formed, which was filtered and dried *in vacuo*. Yield: 0.57 g (82%), mp 95–97 °C. ^{1}H NMR (DMSO-d_6): δ 1.85, 2.15 (s, s, 6H, 6H, CH_3), 5.48 (s, 4H, CH_2), 5.99 (s, 2H, H^4 of pyrazole), 7.28 (d, J = 7.4 Hz, 2H), 7.52–7.58 (m, 2H), 7.68 (s, 2H), 7.74–7.91 (m, 10H) (C_6H_4 and protons of imidazole), 9.43 (s, 2H, protons of imidazolium) ppm. ^{13}C NMR (DMSO-d_6): δ 11.0, 12.9 (CH_3), 51.8 (CH_2), 106.5 (C^4 of pyrazole), 122.4, 124.0, 127.5, 128.2, 128.4, 128.6, 129.9, 130.0, 131.2, 131.6, 134.1, 135.1, 137.3, 141.1, 149.1 (C_6H_4, carbons of imidazole and pyrazole) ppm. Anal. Calc. for $C_{36}H_{36}F_{12}N_8P_2$: C, 49.66; H, 4.17; N, 12.87. Found: C, 49.63; H, 4.17; N, 12.81%.

3.16. Synthesis of $(LH)CH_2C_6H_4CH_2(LH)(BF_4)_2$ (**16**)

This compound was obtained similarly using NH_4BF_4 instead of KPF_6 as described above for **15** as colorless solids. Yield: 83%, mp 54–56 °C. ^{1}H NMR: δ 2.03, 2.04 (s, s, 6H, 6H, CH_3), 5.40 (s, 4H, CH_2), 5.92 (s, 2H, H^4 of pyrazole), 6.92 (s, 2H), 7.28–7.30 (m, 1H), 7.43–7.50 (m, 4H), 7.59 (s, 2H), 7.63–7.68 (m, 4H), 7.56–7.80 (m, 3H) (C_6H_4, C_6H_5 and protons of imidazole), 8.96 (s, 2H, protons of imidazolium) ppm. ^{13}C NMR: δ 11.1, 13.3 (CH_3), 53.0 (CH_2), 107.3 (C^4 of pyrazole), 122.9, 123.2, 126.7, 129.2, 129.9, 130.3, 130.4, 130.8, 131.3, 131.5, 133.7, 134.2, 135.9, 141.6, 150.8 (C_6H_4, C_6H_5, carbons of imidazole and pyrazole) ppm. Anal. Calc. for $C_{36}H_{36}B_2F_8N_8$: C, 57.32; H, 4.81; N, 14.85. Found: C, 56.82; H, 5.26; N, 14.78%.

3.17. Synthesis of $(L)CH_2C_6H_4CH_2(L)Ag_2(PF_6)_2$ (**17**)

This compound was obtained similarly using **15** instead of **7** as described above for **11** as colorless solids. The reaction was 48 h. Yield: 51%, mp 167–169 °C. ^{1}H NMR (DMSO-d_6): δ 1.96, 2.30 (s, s, 6H, 6H, CH_3), 5.34 (d, J = 14.9 Hz, 2H), 5.53 (d, J = 14.9 Hz, 2H) (CH_2), 6.35 (s, 2H, H^4 of pyrazole), 6.89 (s, 2H), 7.46–7.55 (m, 6H), 7.64–7.71 (m, 6H), 7.74–7.78 (m, 2H) (C_6H_4 and protons of imidazole) ppm. ^{13}C NMR (DMSO-d_6): δ 11.6, 13.8 (CH_3), 54.3 (CH_2), 107.0 (C^4 of pyrazole), 121.7, 124.7, 126.9, 127.2, 128.0, 129.0, 130.1, 131.1, 131.4, 132.0, 136.1, 136.8, 145.5, 151.9 (C_6H_4, carbons of imidazole and pyrazole) ppm. The carbene carbon was not observed. Anal. Calc. for $C_{36}H_{36}Ag_2F_{12}N_8P_2.CH_2Cl_2$: C, 38.01; H, 3.10; N, 9.58. Found: C, 38.07; H, 3.05; N, 9.40%.

Table 2
Crystal data and refinement parameters for complexes **10**–**13** and **18**.

Compound	**10**	**11**.CH_3CN	**12**	**13**.CH_3CN	**18**.$2CH_3CN$
Formula	$C_{21}H_{20}AgClN_4$	$C_{40}H_{35}Ag_2F_{12}N_9P_2$	$C_{42}H_{40}Ag_2F_{12}N_8P_2$	$C_{44}H_{43}Ag_2B_2F_8N_9$	$C_{40}H_{40}Ag_2B_2F_8N_{10}$
Formula weight	471.73	1147.45	1162.50	1087.23	1050.18
Crystal size (mm)	0.20 × 0.18 × 0.12	0.20 × 0.18 × 0.10	0.20 × 0.18 × 0.12	0.20 × 0.18 × 0.12	0.20 × 0.18 × 0.10
T (*K*)	113(2)	293(2)	113(2)	113(2)	113(2)
λ(MoKα) (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Orthorhombic	Triclinic	Triclinic	Triclinic
Space group	$P2_1/n$	*P*bca	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	11.748(5)	15.061(3)	11.136(5)	11.985(3)	9.549(3)
b (Å)	13.462(6)	19.088(4)	11.602(4)	12.800(3)	11.264(3)
c (Å)	13.692(6)	31.586(6)	19.038(8)	16.621(5)	20.471(6)
α (°)	90	90	78.25(2)	73.03(2)	93.014(6)
β (°)	114.560(5)	90	77.65(2)	83.53(2)	98.037(7)
γ (°)	90	90	75.76(2)	66.92(2)	97.698(3)
V (Å)^3	1969.4(15)	9081(3)	2299.4(17)	2243.6(10)	2154.9(11)
Z	4	8	2	2	2
D_c (g cm^{-3})	1.591	1.679	1.679	1.609	1.619
F(000)	952	4560	1160	1092	1052
μ(mm^{-1})	1.172	1.023	1.011	0.950	0.986
θ Range (°)	1.93-27.91	2.13-26.03	1.11-27.81	1.28-27.89	2.02-25.02
No. of measured reflections	20,209	72,192	23,501	25,912	17,061
No. of unique reflections (R_{int})	4699 (0.0388)	8925 (0.0699)	10,689(0.0523)	10,575 (0.0356)	7600 (0.0333)
No. of observed reflections with ($I > 2\sigma(I)$)	3724	6315	6350	8517	5773
No. of parameters	246	698	599	628	565
GOF	1.012	1.053	1.001	0.974	1.046
Residuals *R*, *R*w	0.0232, 0.0559	0.0530, 0.1315	0.0395, 0.0660	0.0289, 0.0552	0.0349, 0.0971

3.18. Synthesis of (L)$CH_2C_6H_4CH_2$(L)$Ag_2(BF_4)_2$ (**18**)

This compound was obtained similarly using **16** instead of **7** as described above for **11** as yellow solids. The reaction time was 48 h. Yield: 48%, mp 142–144 °C. ^{1}H NMR (DMSO-d_6): δ 1.96, 2.30 (s, s, 6H, 6H, CH_3), 5.34 (d, J = 14.8 Hz, 2H), 5.53 (d, J = 14.8 Hz, 2H) (CH_2), 6.35 (s, 2H, H^4 of pyrazole), 6.89 (s, 2H), 7.46–7.54 (m, 6H), 7.64–7.70 (m, 6H), 7.74–7.78 (m, 2H) (C_6H_4 and protons of imidazole) ppm. ^{13}C NMR (DMSO-d_6): δ 11.6, 13.8 (CH_3), 54.4 (CH_2), 106.9 (C^4 of pyrazole), 121.7, 124.5, 126.8, 127.2, 128.0, 128.9, 130.4, 131.1, 131.3, 131.9, 136.1, 136.8, 145.6, 151.8 (C_6H_4, carbons of imidazole and pyrazole) ppm. The carbene carbon was not observed. Anal. Calc. for $C_{36}H_{34}Ag_2B_2F_8N_8$.0.5$CH_2Cl_2$: C, 43.38; H, 3.49; N, 11.09. Found: C, 43.76; H, 3.34; N, 10.99%.

3.19. Crystal structure determinations

Crystals of **10** and **12** suitable for X-ray analyses were obtained by slow diffusion of ethyl ether into their CH_2Cl_2 solutions at 4 °C. While crystals of **11**, **13** and **18** suitable for X-ray analyses were obtained by slow diffusion of ethyl ether into their CH_3CN solutions at 4 °C. Crystals of **11** contained one CH_3CN molecule. All fluorine atoms in this complex were found to be disordered. Satisfactory results were obtained when F(1)–F(6) were given occupancy factors of 0.717 and F(1)′–F(6)′ were given occupancy factors of 0.283, as well as 0.688 for F(7)–F(12) and 0.312 for F(7)′–F(12)′, respectively. Crystals of **13** also contained one CH_3CN molecule. The F(5)–F(8) atoms were disordered in **13**. The occupancy factors were refined to 0.826 for F(5)–F(8) and 0.174 for F(5)′–F(8)′, respectively. In addition, crystals of **18** contained two CH_3CN molecules. All intensity data were collected on a Rigaku Saturn CCD detector. Semi-empirical absorption corrections were applied using the Crystalclear program [47]. The structures were solved by direct methods and difference Fourier map using SHELXS of the SHELXTL package and refined with SHELXL [48] by full-matrix least-squares on F^2. All non-hydrogen atoms were refined anisotropically. A summary of the fundamental crystal data for **10**–**13** and **18** is listed in Table 2.

3.20. General procedure for the Ag–NHC catalyzed three-component coupling reaction

In a typical experiment, the mixture of aldehyde (1 mmol), phenylacetylene (1.5 mmol, 164.7 μl), piperidine (1.2 mmol, 118.7 μl), and NHC–Ag complex (n mmol) was charged in the reaction tube (10 ml) with 2 ml of 1,4-dioxane. After the reaction mixture was stirred at 80 °C for given time under Ar atmosphere, the volatile materials were removed under reduced pressure, and the products were purified by column chromatography on silica using ethyl acetate/hexane (1/2 v/v) as the eluent to give the corresponding propargylic amine.

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Appendix A. Supplementary material

CCDC 898717–898721 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.

Appendix B. Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.jorganchem.2012.12.008. These data include MOL files and InChiKeys of the most important compounds described in this article.

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