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A direct and practical approach for the synthesis of *N*-heterocyclic carbene coinage metal complexes

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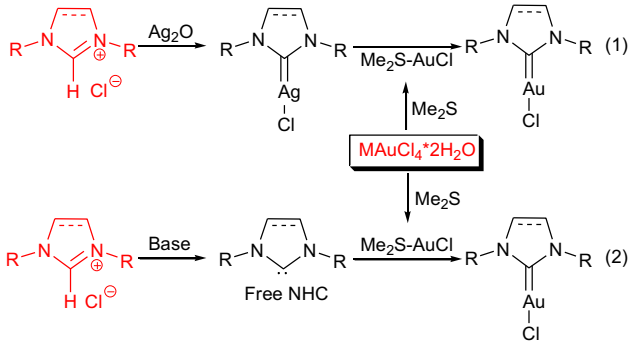
ABSTRACT

A novel direct and practical synthetic route leading to *N*-heterocyclic carbene coinage metal complexes has been developed by using air stable, commercial available Au(III) salt [$MAuCl_4 \cdot 2H_2O$], $CuCl_n$ (n=1,2) or AgCl, and imidazolium salts as starting materials. The reaction proceeded without sacrificing carbene transfer agent (Ag_2O) or using highly sensitive free NHC.

1. Introduction

Group 11 elements (Cu, Ag, Au), conventionally called as coinage metals, have aroused intense interest in the past decades.[1] Gold, unlike its homolog Cu and Ag, known as an inert coinage metal, has attracted more and more interests due to its unexpected catalytic capabilities in the past decade.[1] Both inorganic gold salts and organic gold coordination complexes have been used extensively in various organic transformations.[2] Especially in recent years, it has been found that gold could form stable coordination complexes with *N*-heterocyclic carbene (NHC) ligands.[3] In particular, Au(I)–NHC, which has been successfully used as catalysts in many important reactions, such as nucleophilic additions, Friedel–Crafts reactions, C–H activations, hydrogenations, cross-coupling reactions, and oxidations.[3b–e] In the literature,[4] there are two common ways to synthesize these Au(I)–NHC complexes: (1) using the silver oxide (Ag_2O) route developed by Lin[4a] to generate the appropriate [Ag(NHC)Cl] complexes[4b] that are then used as NHC transfer agents to react with the [Au(DMS)Cl] (DMS=dimethylsulfide),[4c] or (2) free NHC react with the [Au(DMS)Cl][4c] (Scheme 1). [Au(DMS)Cl], which is slightly unstable, was often prepared freshly from gold(III) salts [$MAuCl_4 \cdot 2H_2O$] and used immediately. Therefore, both approaches are actually started from the same starting materials: imidazolium salts and [$MAuCl_4 \cdot 2H_2O$]. These approaches hold the following disadvantages: (a) three-step reaction required for each method to form Au(I)–NHC from the imidazolium salts and gold(III) salts; (b) 1 equiv of expensive Ag_2O is sacrificed as the carbene transfer agent in Eq. 1, which is not desirable in terms of both green chemistry and atom efficiency; (c) isolation of the highly sensitive and unstable free NHC is required for Eq. 2, which is operationally troublesome.



Scheme 1. Conventional ways to synthesize of Au(I)–NHC.

In this context, developing a direct and practical approach without sacrificing carbene transfer agent (Ag_2O) or using highly sensitive starting material (free NHC) to synthesize the important and useful Au(I)–NHC complexes would be highly desirable. Herein, we would like to report a direct and practical one-step

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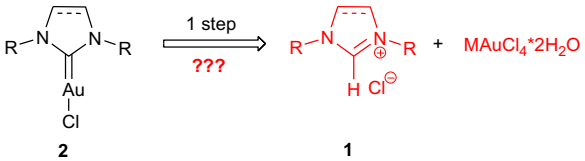
procedure to synthesize Au(I)–NHC complex, this method can also be extended to prepare other coinage metal (Ag and Cu) complexes.

At the outset of the project, we targeted to synthesize Au(I)–NHC from the imidazolium salts and gold(III) salts. Gold(III) is well known for its strong oxidizing character,[5] and in fact, could be easily reduced into gold(I) complexes in the presence of sulfide, phosphine or other organic and inorganic reductants.[5,6] Therefore, we then speculated that it is possible to use the stable and commercially available gold(III) salts [$MAuCl_4 \cdot 2H_2O$], instead of the slightly unstable [Au(DMS)Cl], as the gold source to react with the imidazolium salts directly to prepare the Au(I)–NHC complexes in one step (Scheme 2).



Scheme 2. The retrosynthetic analysis of Au(I)–NHC.

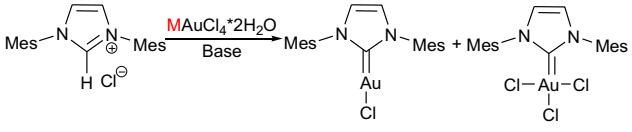
2. Results and discussion

2.1. Synthesis of NHC–AuCl and NHC–$AuCl_3$ complexes

Initial efforts were made to systematically investigate various metalation conditions, using IMes·HCl (**1a**) as the model substrate and [$NaAuCl_4 \cdot 2H_2O$] or [$KAuCl_4 \cdot 2H_2O$] as gold(III) salt (Table 1).

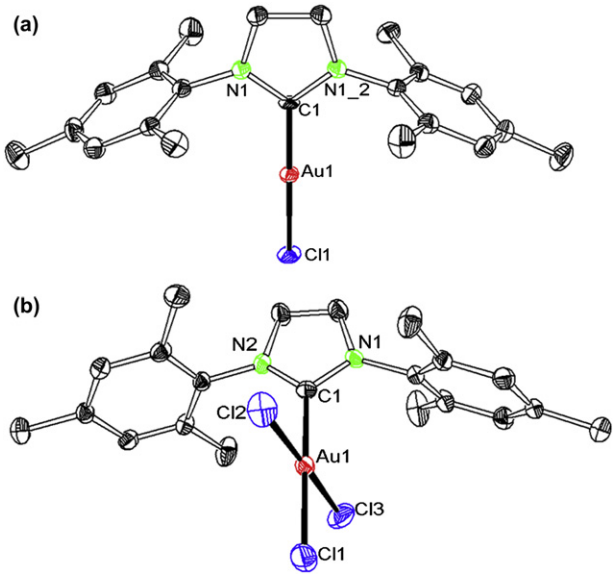
Firstly, different solvents were tested for the reactions when [$NaAuCl_4 \cdot 2H_2O$] was used as the gold source and Na_2CO_3 as the base. When toluene was used as the solvent, a mixture of IMes–AuCl (**2a**) and IMes–$AuCl_3$ (**3a**) was obtained in 53% total yield, with **3a** (40%) being dominated (entry 1, Table 1). When dichloroethane (DCE) was used instead, the yield of IMes–AuCl was increased to 36%, however, the reaction conversion was still low (52%) (entry 2). Trace IMes–AuCl **2a** was observed when the reaction was performed in THF (entry 3). When pyridine was used as the solvent, the ratio of IMes–AuCl (**2a**) to IMes–$AuCl_3$ (**3a**) equals to 1:1, but the overall yield is up to 88% (entry 4). It is surprising that when 3-Cl–pyridine was used as the solvent, IMes–AuCl (**2a**) could be formed solely in 93% yield. No IMes–$AuCl_3$ (**3a**) was detected (entry 5). It is worthy to note that the reaction was not sensitive to water because there are two crystal water in each [$MAuCl_4 \cdot 2H_2O$] molecule. To further figure out the effect of the water, a mixed solvent (3-Cl–pyridine/H_2O=5:1) was employed, the yield of **2a** was still up to 81% (entry 6). When H_2O was served as the sole solvent, however, the yield of **2a** drop to 14% (entry 7). Therefore, 3-Cl–pyridine has proved to be the solvent of choice. Besides the combination of [$NaAuCl_4 \cdot 2H_2O$] and Na_2CO_3, other combinations of gold(III) salts and bases were also investigated (entries 8–10). It is interesting that both [$KAuCl_4 \cdot 2H_2O$]/Na_2CO_3 and [$NaAuCl_4 \cdot 2H_2O$]/K_2CO_3 gave the mixtures of **2a** and **3a** (entries 8 and 9). It is worthy to mention that IMes–$AuCl_3$ (**3a**) could be formed in 60% yield when the former combination was applied. The results here provided an alternative and straightforward way to prepare Au(III)–NHC complexes, which were often indirectly obtained by oxidation of the corresponding Au(I)–NHC with Cl_2 or Br_2.[7] The combination of [$KAuCl_4 \cdot 2H_2O$] with K_2CO_3 could furnish the IMes–AuCl (**2a**) selectively as well, albeit in relatively low yield (65%) (entry 10). Different bases were also investigated: Cs_2CO_3 gave only moderate yield of product **2a** (entry 11). K_3PO_4 produced **2a** in 72% yield, however, accompanying with **3a** in 12% yield (entry 12). NaOH was inefficient for this reaction at all (entry 13). In addition, the reactions did not occur in the absence of the base (entry 14). The structures of IMes–AuCl (**2a**) and IMes–$AuCl_3$ (**3a**) were verified by the single-crystal X-ray diffraction analysis (Scheme 3). Selected bond distances and bond angles are given in the figure caption. The gold atom in **2a** is two-coordinated, as is usual for gold(I) complexes, and exhibits a linear geometry with a C(1)–Au(1)–Cl(1) bond angle value of 180.0°. The Au(1)–C(1) bond length (1.916 Å) in structure **2a** is in good agreement with those reported NHC–gold(I)

Table 1
One step to synthesize Au(I)–NHC complexes from imidazolium salts and commercially available Au(III) salts[a]



Entry	Gold source	Base	Sol	Yield[b]	
				2a (%)	**3a** (%)
1	$NaAuCl_4 \cdot 2H_2O$	Na_2CO_3	Toluene	13	40
2	$NaAuCl_4 \cdot 2H_2O$	Na_2CO_3	DCE[c]	36	16
3	$NaAuCl_4 \cdot 2H_2O$	Na_2CO_3	THF	Trace	—
4	$NaAuCl_4 \cdot 2H_2O$	Na_2CO_3	Pyridine	44	44
5	$NaAuCl_4 \cdot 2H_2O$	Na_2CO_3	3-Cl–pyridine	93	—
6[d]	$NaAuCl_4 \cdot 2H_2O$	Na_2CO_3	3-Cl–pyridine	81	—
7	$NaAuCl_4 \cdot 2H_2O$	Na_2CO_3	H_2O	14[e]	—
8	$KAuCl_4 \cdot 2H_2O$	Na_2CO_3	3-Cl–pyridine	28	60
9	$NaAuCl_4 \cdot 2H_2O$	K_2CO_3	3-Cl–pyridine	59	24
10	$KAuCl_4 \cdot 2H_2O$	K_2CO_3	3-Cl–pyridine	65	—
11	$NaAuCl_4 \cdot 2H_2O$	Cs_2CO_3	3-Cl–pyridine	50	—
12	$NaAuCl_4 \cdot 2H_2O$	K_3PO_4	3-Cl–pyridine	72	12
13	$NaAuCl_4 \cdot 2H_2O$	NaOH	3-Cl–pyridine	—	—
14	$NaAuCl_4 \cdot 2H_2O$	—	3-Cl–pyridine	—	—

[a] Reactions were carried out in a Schlenk tube using **1** (0.15 mmol), [$MAuCl_4 \cdot 2H_2O$] (0.14 mmol), and 0.5 ml 3-Cl–pyridine in a Schlenk tube, heating at 80 °C under the atmosphere of N_2 for 24 h.
[b] isolated yield, the ratio of **2a** to **3a** was determined by ^1H NMR.
[c] DCE (Dichloroethane).
[d] 3-Cl–pyridine/H_2O (5:1) as the solvent.
[e] Determined by ^1H NMR.

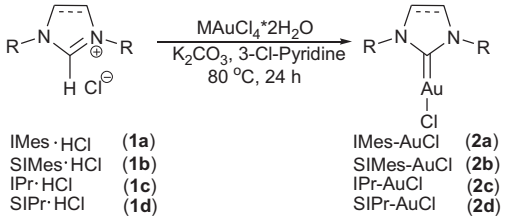


Scheme 3. ORTEP diagram (a) IMes–AuCl **2a** and (b) IMes–$AuCl_3$ **3a**. Selected bond distances (Å) and angles (°) in **2a**: Au(1)–C(1), 1.916(19); Au(1)–Cl(1), 2.285(5); C(1)–Au(1)–Cl(1), 180.000(2). Selected bond distances (Å) and angles (°) in **3a**: Au(1)–C(1), 2.016(7); Au(1)–Cl(1), 2.299(2); Au(1)–Cl(2), 2.281(3); Au(1)–Cl(3), 2.262(3)); C(1)–Au(1)–Cl(1), 178.4(2); C(1)–Au(1)–Cl(2), 88.25(19); C(1)–Au(1)–Cl(3), 91.29(19); Cl(2)–Au(1)–Cl(3) 178.63(10).

complexes.[7b,8] The bond distance of Au(1)–C(1) in **3a** is 2.016 Å, which is also in close agreement with those reported organogold–(III) complexes.[7b,9] The C(1)–Au(1)–Cl(1) and Cl(2)–Au(1)–Cl(3) bonds are nearly linear, with angles between 178.4° and 178.6°.

With the optimized reaction conditions on hand, we then explored its potential substrates scope. Four most common imidazolium salts **1a**–**d** were tested under the standard conditions. All of them gave very satisfied results (Table 2). In order to obtain better results, small modifications were made for each substrate. For example, [$NaAuCl_4 \cdot 2H_2O$] was better than [$KAuCl_4 \cdot 2H_2O$] in the case of imidazolium salt **1a** (Table 1). For salts **1b**–**d**, [$KAuCl_4 \cdot 2H_2O$] has proven better than [$NaAuCl_4 \cdot 2H_2O$]. Moreover, increasing the reaction temperature from 80 to 110 °C could enhance the yield further (**2d** in Table 2). Under the reaction conditions list in Table 2, no Au(III)–NHC complexes were detected or isolated for the substrates **1b**,**c** and **1d**.

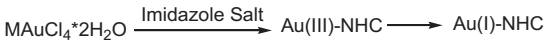
Table 2
One step to synthesize Au(I)–NHC complexes from imidazolium salts and commercially available Au(III) salts[a]



IMes–AuCl (**2a**)	Yield=93%[b]
SIMes–AuCl (**2b**)	Yield=72%[b]
	Yield=91%[c]
IPr–AuCl (**2c**)	Yield=83%[b]
	Yield=89%[c]
SIPr–AuCl (**2d**)	Yield=52%[b]
	Yield=60%[c]
	Yield=74%[d]

[a] Reactions were carried out using **1** (0.15 mmol), [$MAuCl_4 \cdot 2H_2O$] (0.14 mmol), and 0.5 ml 3-Cl–pyridine in a Schlenk tube, heating at 80 °C under the atmosphere of N_2 for 24 h, the yield refers to isolated yield.
[b] [$NaAuCl_4 \cdot 2H_2O$] as the gold source, and Na_2CO_3 as the base.
[c] [$KAuCl_4 \cdot 2H_2O$] as the gold source, and Na_2CO_3 as the base.
[d] The reaction was set at 110 °C for 24 h using [$KAuCl_4 \cdot 2H_2O$] as the gold source, and Na_2CO_3 as the base.

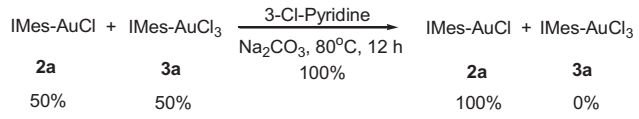
Based on the results listed in Table 1, the reaction could go through the following pathway: Au(III)–NHC formed initially, which was then reduced to Au(I)–NHC under the reaction conditions (Scheme 4).



Scheme 4. Possible pathway for the formation of Au(I)–NHC.

To verify the above hypothesis, a control reaction was designed (Scheme 5). In the presence of 3-chloropyridine and Na_2CO_3, equal molar mixture of IMes–AuCl (**2a**) and IMes–$AuCl_3$ (**3a**) was stirred for 12 h at room temperature and it was found that IMes–$AuCl_3$ (**3a**) was converted completely into IMes–AuCl (**2a**). This observation indicated that gold(III)–NHC could be easily converted into gold(I)–NHC under the reaction conditions.

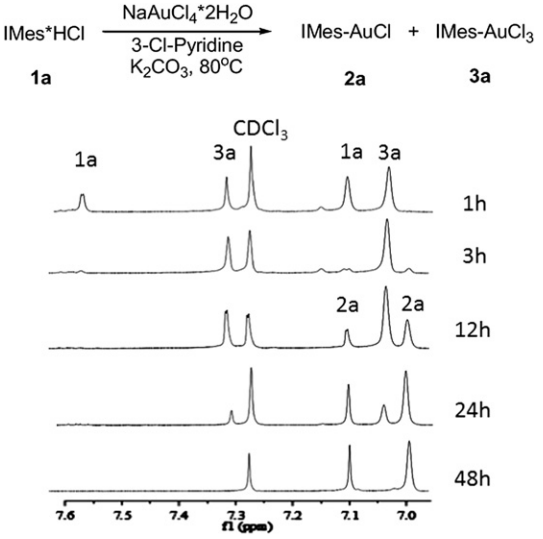
Based on the above results, it comes to us to consider the possibility to selectively prepare gold(III)–NHC by varying the reaction conditions. By careful controlling the reaction conditions, IMes–$AuCl_3$ (**3a**) could be formed in 89% selectivity, accompanying with small amount of unreacted imidazoloium salt **1a** (4%) and



Scheme 5. The control reaction.

reduced product IMes–AuCl **2a** (7%)(Table 3, entry 2). Shorter or longer time resulted in more starting material **1a** or more IMes–AuCl **2a** (entries 1, 3–4). When the reaction time prolongs to 48 h, all of the starting materials were converted into IMes–AuCl **2a** (entry 5). The time-dependent results undoubtedly supported the hypothesis that Au(III)–NHCs were formed initially, which were then reduced further to Au(I)–NHCs under the reaction conditions.

Table 3
Time-dependent of the formation of IMes–$AuCl_3$ (**3a**)



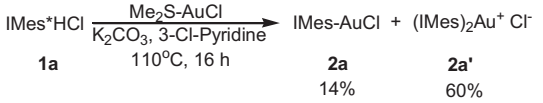
Entry	Reaction time (h)	Product distribution[a]		
		1a	**2a**	**3a**
1	1	23%	—	77%
2	3	4%	7%	89%
3	12	—	27%	73%
4	24	—	71%	29%
5	48	—	100%	—

[a] Product ratios were determined by ^1H NMR. And the reaction was set under the atmosphere of N_2.

Interestingly, when Au(DMS)Cl (DMS=dimethylsulfide) was served as the metalation reagent to react with IMes·HCl, a linear [Au-(IMes)$_2$]$^+$ cation gold complex (**2a′**) was obtained as the major product (60%) instead (Scheme 6), the desired product IMes–AuCl (**2a**) was formed only in 14% yield.

2.2. Synthesis of NHC–CuCl

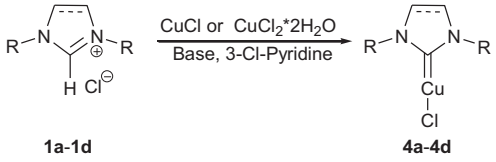
After developing the unique procedure for the synthesis of Au(I)–NHC complex, we were then wondering if this method could be extended to synthesize NHC–CuCl or NHC–AgCl.



Scheme 6. The reaction of IMes·HCl with Me_2S–AuCl.

As summarized in Table 4, CuCl could furnish the desired products NHC–CuCl in excellent yields, the yields are typically

Table 4
Preparation of Cu(I)–NHC complexes[a]

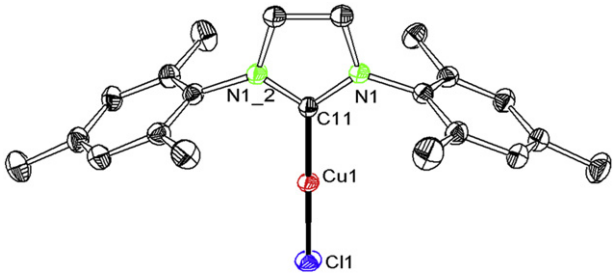


1a-1d 4a-4d

Product	Copper source	Base	Temp (°C)	Yield[b] (%)
IMes–CuCl (**4a**)	CuCl	Na_2CO_3	80	90
	$CuCl_2\cdot 2H_2O$	Na_2CO_3	80	83
SIMes–CuCl (**4b**)	CuCl	K_2CO_3	110	70
	$CuCl_2\cdot 2H_2O$	Na_2CO_3	110	62
IPr–CuCl (**4c**)	CuCl	K_2CO_3	110	99
	$CuCl_2\cdot 2H_2O$	K_2CO_3	110	89
SIPr–CuCl (**4d**)	CuCl	K_2CO_3	110	91
	$CuCl_2\cdot 2H_2O$	K_2CO_3	110	70

[a] The reaction was set under the atmosphere of N_2 for 24 h.
[b] Isolated yield.

ranging from 70 to 99%. Furthermore, $CuCl_2\cdot 2H_2O$, with two crystal water each molecule, could give the same NHC–CuCl as well. As Au(III) being reduced into Au(I), the Cu(II) was also reduced into Cu(I).[10] Different with the gold analogous, no NHC–$CuCl_2$ was isolated or detected. In general, CuCl gave higher yields than $CuCl_2\cdot 2H_2O$. The products from $CuCl_2\cdot 2H_2O$ was also confirmed by X-ray diffraction analysis (Scheme 7). Selected bond distances and bond angles are given in the figure caption. The copper atom is two-coordinated with Cu(1)–C(11) bond distance being 1.898 Å. C(11)–Cu(1)–Cl(1) is also in linear geometry with a bond angle value of 180.0°.



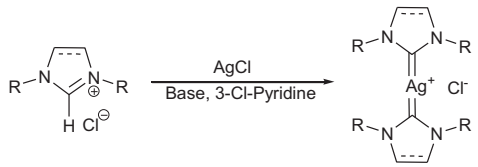
Scheme 7. ORTEP diagram of IMes–CuCl **4a**. Selected bond distances (Å) and angles (°) in **4a**: Cu(1)–C(11), 1.898(6); Cu(1)–Cl(1), 2.0914(17); C(1)–Cu(1)–Cl(1), 180.000(1).

2.3. Synthesis of NHC–AgCl

After the success of applying this system to the synthesis of Cu–NHC, this unique process was further investigated for the Ag–NHC complexes. It is well known that silver transmetalation is a well-established method for the preparation of [(NHC)M] complexes. Although Ag–NHC complexes are typically synthesized from the reaction of imidazolium salts and Ag_2O,[4a] however, the system usually required shielding from the light. Furthermore, silver chloride, AgCl, was often a side-product when scavenging the halide with silver salts in the reactions. Rare applications of AgCl were found in organic synthesis because of its lower stability and insolubility in most organic solvent. Therefore, it is challenging to make use of the AgCl directly in organic chemistry. However, with the success in preparing the corresponding NHC gold and copper complex, we are highly curious about the possibility that if AgCl could be directly used as the silver source to prepare Ag–NHC.

Under the similar conditions, silver chloride was chosen as the metal source, imidazolium salts **1a**–**d** were tested as the substrates for the metallization. As summarized in Table 5, the corresponding

Table 5
Preparation of $(NHC)_2Ag^+Cl^-$ complexes[a]

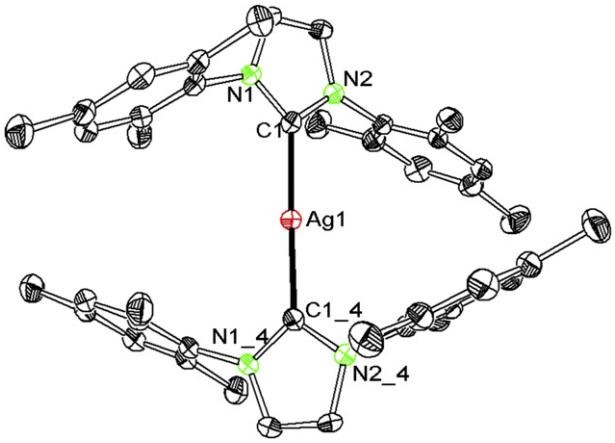


1a-1d 5a-5d

Product	Base	Temp (°C)	Yield[b] (%)
$(IMes)_2Ag^+Cl^-$ (**5a**)	Na_2CO_3	80	83
$(SIMes)_2Ag^+Cl^-$ (**5b**)	K_2CO_3	110	60
$(IPr)_2Ag^+Cl^-$ (**5c**)	K_2CO_3	110	94
$(SIPr)_2Ag^+Cl^-$ (**5d**)	K_2CO_3	110	99

[a] The reaction was set under the atmosphere of N_2 for 24 h.
[b] Isolated yield.

Ag–NHC complexes could be formed efficiently (83–99%) under the standard reaction conditions, except in the case of **5b** (60%). However, the X-ray diffraction analysis of **5a** revealed that the structures of **5** was different with the corresponding gold and copper analogues **2** and **4**, it consists of a linear [Ag-$(IMes)_2$]$^+$ cation and a chloride anion, with one silver ligated to two NHC ligands (Scheme 8). Selected bond distances and bond angles are given in

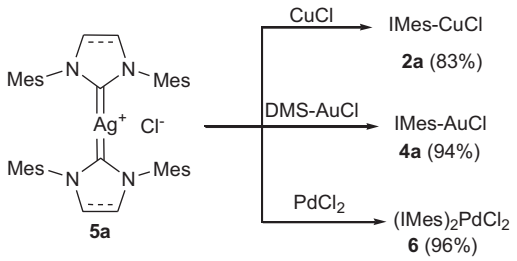


Scheme 8. ORTEP diagram of $(IMes)_2Ag^+Cl^-$ **5a**. Selected bond distances (Å) and angles (°) in **5a**: Ag(1)–C(1), 2.087(4); C(1)–Ag(1)–C (1_4), 178.2(3).

the figure caption. Among which, Ag(1)–C(1) bond distance is 2.087 Å. The C(1)–Ag(1)–C(1_4) is also nearly linear, with angle of 178.2°. Two planes of the imidazolium ring are staggered in an angle of 121.36°.

2.4. Transmetalation from $(NHC)_2Ag^+Cl^-$ complexes

Silver transmetalation is a well-established method for the preparation of [(NHC)M] complexes. Therefore, with $Ag(NHC)_2]^+Cl^-$ **5** on hand, we further explored the carbene transfer reactions. Using dichloromethane as the solvent, CuCl, DMS–AuCl, and $PdCl_2$ could be transmetallated with **5a** smoothly. The corresponding metal complexes **2a**, **4a**, and **6** could be formed in excellent yields (Scheme 9).



Scheme 9. Transmetalation from $(IMes)_2AgCl$ **5a**.

3. Conclusion

In summary, we described a direct and practical approach for the synthesis of Au(I)–NHC complexes from imidazolium salts and commercially available Au(III) salts. This process proceeded without sacrificing carbene transfer agent (Ag_2O) or using highly sensitive free NHC. The control reaction proved that the Au(III)–NHC complexes were formed initially, which were then reduced to Au(I)–NHC under the reaction conditions. Furthermore, this system could also be extended to copper and silver as well. In the case of copper, both CuCl and $CuCl_2\cdot 2H_2O$ furnished the same products NHC–CuCl in good to excellent yields. And for the silver, AgCl could be used as the metal source. Different with gold and copper partners, AgCl gave a linear and ion complex $[Ag(NHC)_2]^+Cl^-$, with one silver ligated to two NHC ligands. The reactions described in this paper are not sensitive to the air, moisture, and light. We believed that, owing to the above advantages, these metalation methods will be the choice for the synthesis of gold, silver, and copper NHC complexes, especially for the gold–NHC. Work to expand the scope and applying the method to other transitional metals is currently underway in our laboratory.

4. Experimental section

4.1. General considerations

All glassware was oven-dried prior to use. All reagents were purchased from commercial sources and used without further purification. Imidazolium salts were prepared according to literature. ^1H and ^{13}C spectra were recorded at 400 MHz and 100 MHz, respectively, on a Bruker Spectrospin 400 MHz spectrometer. Proton and carbon chemical shifts were referenced to the residual proton resonance in $CDCl_3$ (δ (ppm) 7.26 and 77.16, respectively).

4.2. Crystal data of 2a, 3a, 4a, and 5a

Crystal data of **2a**: CCDC No. 824114, $C_{21}H_{24}AuClN_2$, M_r=536.84, colorless block, a=14.766(3), b=29.218(6), c=9.7341(19) Å, α=90, β=90, γ=90°, V=4199.6(14) Å^3, Z=8, D_c=1.698 g/cm^3, T=293(2) K. 2373 unique reflections [R(int)=0.0575]. F(000)=2080 Final R_1 [with $I>2\sigma(I)$]=0.0342, wR_2 (all data)=0.0874. Crystal data of **3a**: CCDC No. 824115, $C_{21}H_{24}AuCl_3N_2$, M_r=607.74, colorless block, a=10.596(2), b=13.932(3), c=15.456(3) Å, α=90, β=90, γ=90°, V=2281.6(8), Z=4, D_c=1.769 g/cm^3, T=293(2) K. 5214 unique reflections [R(int)=0.0951]. F(000)=1176, Final R_1 [with $I>2\sigma(I)$]=0.0448, wR_2 (all data)=0.1127. Crystal data of **4a**: $C_{21}H_{24}ClCuN_2$, M_r=403.41, colorless block, a=14.743(3), b=29.395(6), c=9.5209(19) Å, α=90, β=90, γ=90°, V=4126.0(14) Å^3, Z=8, D_c=1.299 g/cm^3, T=293(2) K. 2366 unique reflections [R(int)=0.0354]. F(000)=1680 Final $R1$ [with $I>2\sigma(I)$]=0.0436, $wR2$ (all data)=0.1274. Crystal data of **5a**: $C_{42}H_{48}AgClN_4$, M_r=752.16, colorless block, a=15.3730(6), b=15.0634(7), c=16.4470(7) Å, α=90, β=90, γ=90°, V=3808.6(3) Å^3, Z=4, D_c=1.312 g/cm^3, T=293(2) K. 3352 unique reflections [R(int)=0.0960]. F(000)=1568 Final $R1$ [with $I>2\sigma(I)$]=0.0461, $wR2$ (all data)=0.1262. The structures were solved by direct methods and refined on F^2 using full matrix least-squares methods using SHELXTL-97. Anisotropic thermal parameters were refined for non-hydrogen atoms within the main backbone of the molecules. Hydrogen atoms were localized in their calculated positions and refined using a riding model.

4.3. Synthesis of imidazol(idin)ium salts

4.3.1. IMes·HCl (**1a**) and SIMes·HCl (**1b**).[11]

4.3.1.1. Preparation of N,N′-(ethane-1,2-diylidene)bis(2,4,6-trimethylaniline). In a flask, 2,4,6-trimethylaniline (6.075 g, 45 mmol) and 40% glyoxylaldehyde (3.250 g, 22.5 mmol) were added to ethyl alcohol (100 ml), the mixture was stirred at room temperature for 12 h and then yellow solid was separated out, the insoluble material was filtered and the filtrate was washed with cold ethyl alcohol, after dried in vacuum, gave 4.7 g yellow solid of imine in 71% yield.

*4.3.1.2. Preparation of IMes·HCl (**1a**).* In a flask, the imine (3.0 g, 10 mmol) was dissolved in tetrahydrofuran (25 ml), followed by dropwise addition of chloromethyl ethyl ether (1.04 g, 11 mmol), the mixture was stirred under N_2 at 40 °C for 18 h, and then ethyl ether (25 ml) was added to separate white solid, the solid was filtered and washed with ethyl ether, the white solid was dried under vacuum affording 2.2 g IMes·HCl in 65% yield. ^1H NMR ($CDCl_3$, 400 MHz): δ 2.15 (s, 12H), 2.33 (s, 6H), 7.00 (s, 4H), 7.70 (s, 2H), 10.73 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 17.6, 21.1, 124.8, 129.8, 130.7, 134.1, 139.2, 141.1.

*4.3.1.3. Preparation of SIMes·HCl (**1b**).* In a flask, the imine (1.3 g, 4.45 mmol) was suspended in ethyl alcohol (65 ml), then cooled to 0 °C and sodium borohydride (3.36 g, 89 mmol) was added slowly, after stirring for 30 min, the mixture was heated to reflux until the color of the solution turn into colorless. Cool to room temperature, then aqueous saturated sodium chloride (12 ml) was added to stir for 30 min, after that, 50 ml water and 40 ml chloroform was added, then organic phase was separated, washed with small amount of water, dried under anhydrous sodium sulfate, and then volatiles were removed under vacuum, yielding light yellow oil. The oil was purged to next step. In the same flask, ammonium chlorite (261.9 mg, 4.9 mmol) and triethyl orthoformate (4 ml) was added, the mixture was stirred under N_2 at 110 °C overnight, then ethyl ether was added to separated yellow solid, filtered and then recrystallized by dichloromethane and ethyl ether, affording 1.3 g yellow SIMes·HCl in 85% yield. ^1H NMR ($CDCl_3$, 400 MHz): δ 2.30 (s, 6H), 2.40 (s, 12H), 4.61 (s, 4H), 6.97 (s, 4H), 7.27 (s, 2H), 9.16 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 17.9, 21.0, 51.9, 129.9, 130.3, 135.0, 140.3, 160.1.

4.3.2. IPr·HCl (**1c**) and SIPr·HCl (**1d**).[11]

4.3.2.1. The preparation of IPr·HCl and SIPr·HCl followed the procedures for the synthesis of IMes·HCl and SIMes·HCl. IPr·HCl (**1c**, 61%): ^1H NMR ($CDCl_3$, 400 MHz): δ 1.22 (d, J=6.4 Hz, 12H), 1.27 (d, J=6.4 Hz, 12H), 2.39–2.46 (m, 4H), 7.34 (d, J=8 Hz, 4H), 7.56 (t, J=8 Hz, 2H), 8.12 (s, 2H), 10.03 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 23.7, 24.7, 29.1, 124.7, 126.8, 129.9, 132.1, 138.5, 145.0.

SIPr·HCl (**1d**, 69%): ^1H NMR ($CDCl_3$, 400 MHz): δ 1.26 (d, J=6.8 Hz, 12H), 1.41 (d, J=6.8 Hz, 12H), 3.00–3.07 (m, 4H), 4.86 (s, 4H), 7.29 (d, J=8 Hz, 4H), 7.48 (t, J=8 Hz, 2H), 8.30 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 23.7, 25.4, 29.2, 55.2, 124.9, 129.3, 131.5, 146.0, 158.7.

4.4. Synthesis of [(NHC)AuCl] (2a–d)[4c]

Based on the conditions listed in Table 4, equal molar of potassium chloroaurate dihydrate (58 mg, 0.14 mmol) or sodium chloroaurate dehydrate (56 mg, 0.14 mmol), the imidazol(idin)ium chloride (0.15 mmol) and potassium carbonate (94 mg, 0.68 mmol) or sodium carbonate (72 mg, 0.68 mmol) were introduced in a Schlenk tube equipped with a magnetic stirring bar. The Schlenk tube was then added 3-chloropyridine (0.5 ml), the reaction mixture was stirred at 80 °Cor 110 °C for the time indicated in Table 4. The Schlenk tube was allowed to cool to room temperature, 1.0 ml dichloromethane was added to dissolve the product, then the mixture passed through a short pad of silica gel, eluting with dichloromethane until all the product coming comes out. Dichloromethane was then removed by rotary evaporator; the residual solution was added to a stirring n-pentane to precipitate solid powders, filtered to afford the corresponding [(NHC)AuCl].

*4.4.1. [(IMes)AuCl] (**2a**)* ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.10 (s, 12H), 2.35 (s, 6H), 6.99 (s, 4H), 7.10 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 17.8, 21.1, 122.2, 129.5, 134.6, 134.7, 139.8, 173.4.

*4.4.2. [(SIMes)AuCl] (**2b**)* ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.30 (s, 6H), 2.32 (s, 12H), 3.99 (s, 4H), 6.94 (s, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 18.0, 21.1, 50.7, 129.8, 134.6, 135.5, 139.0, 195.1.

*4.4.3. [(IPr)AuCl] (**2c**)* ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.21 (d, J=6.8 Hz, 12H), 1.34 (d, J=6.8 Hz, 12H), 2.50–2.61 (m, 4H), 7.17 (s, 2H), 7.28 (d, J=8H, 4 Hz), 7.50 (t, J=8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 24.0, 24.5, 28.8, 123.1, 124.3, 130.7, 134.0, 145.6, 175.3.

*4.4.4. [(SIPr)AuCl] (**2d**)* ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.33 (d, J=6.8 Hz, 12H), 1.41 (d, J=6.8 Hz, 12H), 3.00–3.10 (m, 4H), 4.04 (s, 4H), 7.22 (d, J=7.6 Hz, 4H), 7.41 (t, J=7.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 24.1, 25.1, 29.0, 53.5, 124.6, 130.0, 134.0, 146.5, 196.0.

4.5. Synthesis of [$(IMes)_2Au^+Cl^-$] (2a′)

(Me_2S)AuCl (84 mg, 0.28 mmol) and the IMes·HCl (200 mg, 0.60 mmol) and potassium carbonate (187.7 mg, 1.36 mmol) were introduced in a Schlenk tube equipped with a magnetic stirring bar. To the Schlenk tube was then added 3-chloropyridine (1.0 ml), the reaction mixture was stirred at 110 °C for 16 h, then cool to room temperature, 1.0 ml dichloromethane was added to dissolve the product, then the mixture passed through a short pad of silica gel covered with a pad of Celite eluting with dichloromethane until the product was all obtained. Dichloromethane was removed by rotary evaporator; the residual solution was added to *n*-pentane to precipitate solid powders, filtered and dried, affording the mixture of [(IMes)AuCl] (**2a**) and [$(IMes)_2Au]^+Cl^-$ (**2a′**), the two products were then isolated through column chromatography on silica gel to give 21.0 mg [(IMes)AuCl] (**2a**) in 14% yield and 141 mg [$(IMes)_2Au]^+Cl^-$ (**2a′**) in 60% yield.

*4.5.1. [$(IMes)_2Au]^+Cl^-$ (**2a′**)* ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.70 (s, 12H), 2.44 (s, 6H), 6.89 (s, 4H), 7.17 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 17.1, 21.3, 123.1, 129.1, 134.1, 134.5, 139.4, 185.1.

4.6. Synthesis of [$(IMes)AuCl_3$] (3a)[12]

Sodium chloroaurate dihydrate (56 mg, 0.14 mmol) and, IMes·HCl (50 mg, 0.15 mmol) and potassium carbonate (94 mg, 0.68 mmol) were introduced into a Schlenk tube equipped with a magnetic stirring bar. To the Schlenk tube was then added 3-chloropyridine (0.5 ml), the reaction mixture was stirred at 80 °C for 3 h, the Schlenk tube was allowed to cool to room temperature, 1.0 ml dichloromethane was added to dissolve the product, then the mixture passed through a short pad of silica gel eluting with dichloromethane until the product was all fully obtained. Dichloromethane was removed by rotary evaporator; the residual solution was added to *n*-pentane to precipitate solid powders, after filtered and dried, affording the mixture of [(IMes)AuCl] (**2a**) in 7% yield and [$(IMes)AuCl_3$] (**3a**) in 89% yield (determined by NMR yield). Pure [$(IMes)AuCl_3$] (**3a**) could be obtained by simply diffusion of pentane into the DCM solution of **3a**. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.25 (s, 12H), 2.36 (s, 6H), 7.03 (s, 4H), 7.30 (s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 18.6, 21.2, 125.6, 130.0, 132.4, 135.3, 141.1, 144.8.

4.7. Synthesis of [(NHC)CuCl] (4a–d)[13]

Cuprous chloride (14.0 mg, 0.14 mmol) or cupric dichloride dihydrate (24.0 mg, 0.14 mmol) and, the imidazol(idin)ium chloride (0.15 mmol) and potassium carbonate (93.8 mg, 0.68 mmol) or sodium carbonate (for [(SIMes)CuCl], 72.1 mg, 0.68 mmol) were introduced in a Schlenk tube equipped with a magnetic stirring bar. To the Schlenk tube was then added 3-chloropyridine (0.5 ml), the reaction mixture was stirred at 110 °C for 16 h. Cool to room temperature, 1.0 ml dichloromethane was added to dissolve the product, then the mixture passed through a short pad of silica gel covered with a pad of Celite eluting with dichloromethane until the product was completely washed out. Dichloromethane was then removed by rotary evaporator; the residual solution was added to *n*-pentane to precipitate solid powders, filtered and dried, affording the corresponding [(NHC)CuCl].

*4.7.1. [(IMes)CuCl] (**4a**)* ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.10 (s, 12H), 2.35 (s, 6H), 7.00 (s, 4H), 7.05 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 17.8, 21.1, 122.3, 129.5, 134.6, 135.1, 139.5.

*4.7.2. [(SIMes)CuCl] (**4b**)* ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.30 (s, 6H), 2.32 (s, 12H), 3.95 (s, 4H), 6.95 (s, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 18.0, 21.0, 51.0, 129.8, 134.9, 135.4, 138.7.

*4.7.3. [(IPr)CuCl] (**4c**)* ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.23 (d, J=6.8 Hz, 12H), 1.30 (d, J=6.8 Hz, 12H), 2.51–2.62 (m, 4H), 7.13 (s, 2H), 7.29 (d, J=8 Hz, 4H), 7.49 (t, J=8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 23.9, 24.8, 28.7, 123.2, 124.2, 130.6, 134.4, 145.6, 180.5.

*4.7.4. [(SIPr)CuCl] (**4d**)* ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.34 (d, J=7.2 Hz, 12H), 1.36 (d, J=7.2 Hz, 12H), 3.01–3.11 (m, 4H), 4.01 (s, 4H), 7.23 (d, J=5.2 Hz, 4H), 7.39 (t, J=8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 23.9, 25.5, 28.9, 53.7, 124.5, 130.0, 134.4, 146.6, 202.9.

4.8. Synthesis of [$(NHC)_2Ag]^+Cl^-$ (5a–d)[14]

Silver chloride (20.0 mg, 0.14 mmol), the imidazol(idin)ium chloride (0.15 mmol) and potassium carbonate (93.8 mg, 0.68 mmol) or sodium carbonate (for [(SIMes)CuCl], 72.1 mg, 0.68 mmol) were introduced in a Schlenk tube equipped with a magnetic stirring bar. To the Schlenk tube was then added 3-chloropyridine (0.5 ml), the reaction mixture was stirred at 110 °C for 16 h. Cool to room temperature, 1.0 ml dichloromethane was added to dissolve the product, then the mixture passed through a short pad of silica gel covered with a pad of Celite eluting with dichloromethane until the product was completely washed out. Dichloromethane was removed by rotary evaporator; the residual solution was added to *n*-pentane to precipitate solid powders, filtered and dried, affording the corresponding [$(IMes)_2Ag]^+Cl^-$.

*4.8.1. [(IMes)$_2$Ag]$^+$Cl$^-$ (**5a**)* ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.07 (s, 12H), 2.35 (s, 6H), 7.00 (s, 4H), 7.14 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 17.8, 21.2, 122.8, 122.8, 129.7, 134.7, 135.3, 139.9.

*4.8.2. [(SIMes)$_2$Ag]$^+$Cl$^-$ (**5b**)* ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.29 (s, 6H), 2.30 (s, 12H), 4.00 (s, 4H), 6.95 (s, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 18.0, 21.0, 51.1, 51.2, 129.9, 135.1, 135.5, 138.9.

*4.8.3. [(IPr)$_2$Ag]$^+$Cl$^-$ (**5c**)* ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.22 (d, J=7.2 Hz, 12H), 1.28 (d, J=6.8 Hz, 12H), 2.49–2.59 (m, 4H), 7.21 (d, J=1.6 Hz, 2H), 7.30 (d, J=8 Hz, 4H), 7.50 (t, J=8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 24.0, 24.7, 28.7, 123.6, 123.7, 124.4, 130.8, 134.5, 145.6.

*4.8.4. [(SIPr)$_2$Ag]$^+$Cl$^-$ (**5d**)* ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.33 (d, J=1.2 Hz, 12H), 1.35 (d, J=1.2 Hz, 12H), 3.00–3.10 (m, 4H), 4.07 (s, 4H), 7.24 (d, J=8.0 Hz, 4H), 7.41 (t, J=8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 24.0, 25.4, 28.9, 53.9, 53.9, 124.7, 130.1, 134.5, 146.6.

4.9. Transmetalation from (NHC)$_2$Ag$^+$Cl$^-$ complexes

To a Schlenk tube with a stirring bar, adding [(IMes)$_2$Ag]$^+$Cl$^-$ (0.021 mmol, 15.7 mg) and metal chloride (CuCl, DMS–AuCl or $PdCl_2$) (0.046 mmol), the Schlenk tube system was then added 1.0 ml dichloromethane, the reaction was then stirred at room temperature overnight. After that, the reaction mixture was filtered, and the volatile material was removed by rotary evaporator to obtain products of **2a**, **4a**, and **6**.

*4.9.1. [(IMes)$_2$PdCl$_2$] (**6**).*[15] ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.95 (s, 12H), 2.47 (s, 6H), 6.77 (s, 2H), 6.93 (s, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 18.9, 21.3, 122.5, 122.8, 135.8, 136.2, 137.5, 170.9.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tet.2012.07.009.

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