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# A direct and practical approach for the synthesis of Au(I)-NHC complexes from commercially available imidazolium salts and Au(III) salts

Shifa Zhu<sup>a,b,\*</sup>, Renxiao Liang<sup>a</sup>, Lijuan Chen<sup>a</sup>, Chao Wang<sup>a</sup>, Yanwei Ren<sup>a</sup>, Huanfeng Jiang<sup>a</sup>

<sup>a</sup> School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, China

<sup>b</sup> Faculty of Chemistry & Material Engineering, Wenzhou University, Zhejiang Province, Wenzhou 325027, China

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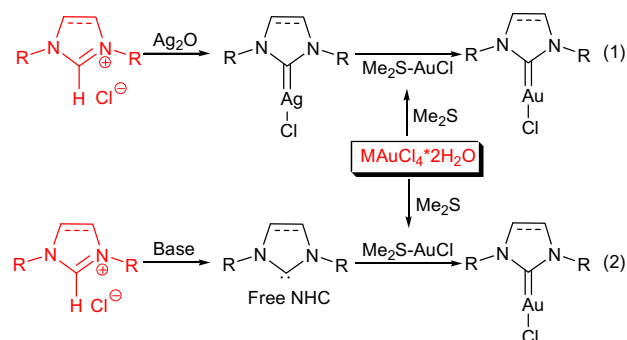
## ABSTRACT

A direct and practical approach for the synthesis of Au(I)-NHC complexes from imidazolium salts and commercially available aurate salt (MAuCl<sub>4</sub>·2H<sub>2</sub>O) is described. The reaction proceeded without sacrificing carbene transfer agent (Ag<sub>2</sub>O) or using highly sensitive free NHC.

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Gold, known as an inert coinage metal, has aroused intense interests in the past decade.<sup>1</sup> Both the inorganic gold salts and the organic gold coordination complexes have been used extensively in various organic transformations.<sup>2</sup> Especially in recent years, it has found that gold can form stable coordination complexes with *N*-heterocyclic carbene (NHC) ligands.<sup>3</sup> In particular, Au(I)-NHC, which has been successfully used as catalysts in many important reactions, for examples, nucleophilic additions, Friedel–Crafts reactions, C–H activations, hydrogenations, and oxidations.<sup>3</sup> In the literature,<sup>4</sup> there are two common ways to synthesize the Au(I)-NHC complexes: (1) using the silver oxide route developed by Lin to generate the appropriate [Ag(NHC)Cl] complexes that are used as NHC transfer agents when reacted with the [Au(DMS)Cl] precursor (DMS = dimethylsulfide) or (2) free NHC react with the [Au(DMS)Cl] (Scheme 1). Both approaches started from the same starting materials: imidazolium salts and aurate salts (MAuCl<sub>4</sub>·2H<sub>2</sub>O). These approaches hold the following disadvantages: (a) three-step reaction required for each method; (b) at least one equivalent of expensive Ag<sub>2</sub>O 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.

In this context, developing a direct and practical approach without sacrificing carbene transfer agent (Ag<sub>2</sub>O) or using highly sensitive starting material (free NHC) to synthesize the important and useful Au(I)-NHC complexes would be highly desirable.



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

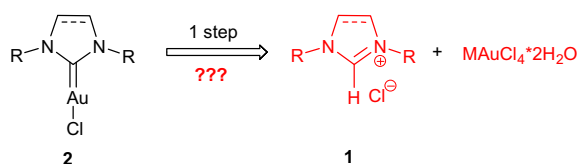
Gold(III), is well known for its very strong oxidant character.<sup>5</sup> In fact, Au(III) could be easily reduced into Au(I) complexes in the presence of sulfide, phosphine and other reductants.<sup>5,6</sup> Therefore, we speculated that it is possible to use the stable and commercially available aurate salts (MAuCl<sub>4</sub>·2H<sub>2</sub>O) instead of the unstable [Au(DMS)Cl] (sensitive to air) as the gold source to react with the imidazolium salts directly to prepare the Au(I)-NHC complexes in one-step (Scheme 2).

Therefore, the primary goal of this Letter is to develop a method to synthesize the Au(I)-NHC in one-step using imidazolium salts and commercially available aurate salts (MAuCl<sub>4</sub>·2H<sub>2</sub>O) as the direct starting materials. Herein, we would like to report the progress we have made on this project.

Initial efforts were made to systematically investigate various metallation conditions using IMes-HCl (**1a**) as the model substrate

\* Corresponding author.

E-mail address: [zhushf@scut.edu.cn](mailto:zhushf@scut.edu.cn) (S. Zhu).



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

and  $\text{MAuCl}_4 \cdot 2\text{H}_2\text{O}$  ( $\text{M} = \text{K}, \text{Na}$ ) as the metal source (Table 1). Started with  $\text{NaAuCl}_4 \cdot 2\text{H}_2\text{O}$  as the gold source and  $\text{Na}_2\text{CO}_3$  as the base, different solvents were screened for the reactions. When toluene was used as the solvent, a mixture of  $\text{IMes-AuCl}$  (**2a**) and  $\text{IMes-AuCl}_3$  (**3a**) were obtained in 53% total yield, with **3a** (40%) being dominant (entry 1, Table 1). These results indicated both Au(III)-NHC and Au(I)-NHC could be formed directly from the imidazolium salts and chloroaurate salts, which encouraged us to examine the reaction conditions carefully to enhance the selectivity of  $\text{IMes-AuCl}$  (**2a**). When DCE was used instead, the yield of  $\text{IMes-AuCl}$  was increased to 36%, however, the reaction conversion (52%) is still low (entry 2). Trace Au(I)-NHC **2a** was observed when the reaction was performed in THF (entry 3). When pyridine was used as the solvent, the ratio of  $\text{IMes-AuCl}$  (**2a**) with  $\text{IMes-AuCl}_3$  (**3a**) equals to 1:1, but the overall yield is excellent (up to 88%) (entry 4). It is surprising that when 3-Cl-pyridine was used as the solvent instead,  $\text{IMes-AuCl}$  (**2a**) could be formed solely in 93% isolated yield. No  $\text{IMes-AuCl}_3$  (**3a**) was detected (entry 5). It is worthy mentioning that the reaction was not sensitive to moisture at all, because two crystal water existed in each  $\text{MAuCl}_4 \cdot 2\text{H}_2\text{O}$  molecule. Even the mixed co-solvent of 3-Cl-pyridine and  $\text{H}_2\text{O}$  (volume ratio = 5:1) could furnish the product **2a** as well, the yield is up to 81% (entry 6). When net  $\text{H}_2\text{O}$  served as the solvent, however, the yield of **2a** decreased to 14% (entry 7), presumably because of the low solubility of the imidazolium salts in water. Therefore, 3-Cl-pyridine has proved to be the solvent of choice for this reaction. Besides the combination of  $\text{NaAuCl}_4 \cdot 2\text{H}_2\text{O}$  and  $\text{Na}_2\text{CO}_3$ ,

other combinations of aurate salts and bases were tested as well (entries 8–10). Interestingly, both  $\text{KAuCl}_4 \cdot 2\text{H}_2\text{O}/\text{Na}_2\text{CO}_3$  and  $\text{NaAuCl}_4 \cdot 2\text{H}_2\text{O}/\text{K}_2\text{CO}_3$  gave the mixtures of **2a** and **3a** (entries 8 and 9). It is worthy to mention that  $\text{IMes-AuCl}_3$  (**3a**) can be formed in 60% yield when the former combination was applied (entries 8). The results here provided an alternative and straightforward way to prepare the Au(III)-NHC complexes, which were often indirectly obtained by oxidation of the corresponding Au(I)-NHC with  $\text{X}_2$  or  $\text{PhICl}_2$ .<sup>7</sup> The combination of  $\text{KAuCl}_4 \cdot 2\text{H}_2\text{O}/\text{K}_2\text{CO}_3$  could furnish the  $\text{IMes-AuCl}$  (**2a**) selectively as well, albeit in relatively lower yield (65%) (entry 10). Different bases were also investigated.  $\text{Cs}_2\text{CO}_3$  gave only moderate yield of product **2a** (entry 11).  $\text{K}_3\text{PO}_4$  produced **2a** in 72% yield, however, accompanied with **3a** in 12% yield (entry 12).  $\text{NaOH}$  was inefficient for this reaction at all (entry 13). In addition, the reactions can not happen without addition of the base (entry 14).

The structures of  $\text{IMes-AuCl}$  (**2a**) and  $\text{IMes-AuCl}_3$  (**3a**) were verified with the single-crystal X-ray diffraction analysis (Scheme 3), which were consistent with the reported data.<sup>4c</sup>

With the optimized reaction conditions (Table 1, entry 5) on hand, we then explored its potential substrates scope. Four most commonly used imidazolium salts **1a–1d** were tested under the standard conditions. All of them could give satisfied results (Table 2). In order to obtain better results, small modifications were made for each substrate. For example,  $\text{NaAuCl}_4 \cdot 2\text{H}_2\text{O}$  was better than  $\text{KAuCl}_4 \cdot 2\text{H}_2\text{O}$  only in the case of imidazolium salt **1a** (Table 1). For salts **1b–1d**,  $\text{KAuCl}_4 \cdot 2\text{H}_2\text{O}$  has been proven better than  $\text{NaAuCl}_4 \cdot 2\text{H}_2\text{O}$ . Moreover, increasing the reaction temperature from 80 °C 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, 1c** and **1d**.

Base on the results observed in Table 1, we proposed that the reaction could go through the following pathway: initially, the imidazolium reacted with aurate salt giving gold(III)-NHC, which was then reduced to the desired gold(I)-NHC under the reaction conditions (Scheme 4).

**Table 1**  
One step to synthesize Au(I)-NHC complexes from imidazolium salts and commercially available Au(III) salts<sup>a</sup>

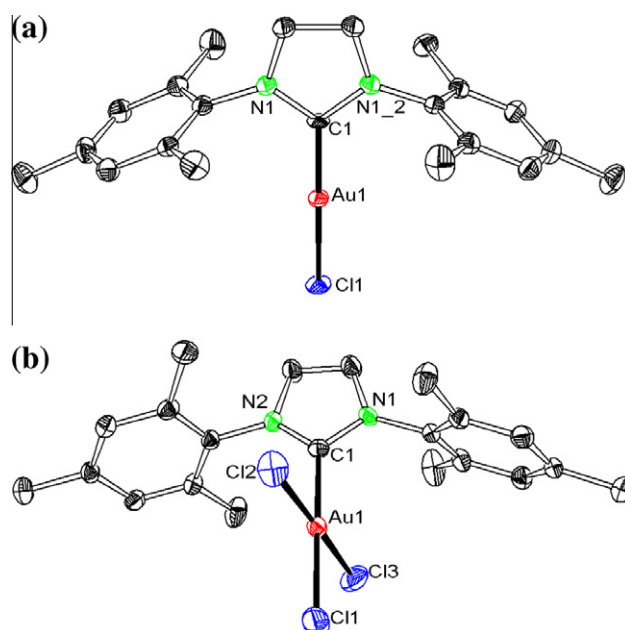
Entry	Gold source	Base	Sol.	Yield <sup>b</sup> (%)	
				<b>2a</b>	<b>3a</b>
1	$\text{NaAuCl}_4 \cdot 2\text{H}_2\text{O}$	$\text{Na}_2\text{CO}_3$	Toluene	13	40
2	$\text{NaAuCl}_4 \cdot 2\text{H}_2\text{O}$	$\text{Na}_2\text{CO}_3$	DCE	36	16
3	$\text{NaAuCl}_4 \cdot 2\text{H}_2\text{O}$	$\text{Na}_2\text{CO}_3$	THF	Trace	—
4	$\text{NaAuCl}_4 \cdot 2\text{H}_2\text{O}$	$\text{Na}_2\text{CO}_3$	Pyridine	44	44
5	$\text{NaAuCl}_4 \cdot 2\text{H}_2\text{O}$	$\text{Na}_2\text{CO}_3$	3-Cl-pyridine	93	—
6 <sup>c</sup>	$\text{NaAuCl}_4 \cdot 2\text{H}_2\text{O}$	$\text{Na}_2\text{CO}_3$	3-Cl-pyridine	81	—
7	$\text{NaAuCl}_4 \cdot 2\text{H}_2\text{O}$	$\text{Na}_2\text{CO}_3$	$\text{H}_2\text{O}$	14 <sup>d</sup>	—
8	$\text{KAuCl}_4 \cdot 2\text{H}_2\text{O}$	$\text{Na}_2\text{CO}_3$	3-Cl-pyridine	28	60
9	$\text{NaAuCl}_4 \cdot 2\text{H}_2\text{O}$	$\text{K}_2\text{CO}_3$	3-Cl-pyridine	59	24
10	$\text{KAuCl}_4 \cdot 2\text{H}_2\text{O}$	$\text{K}_2\text{CO}_3$	3-Cl-pyridine	65	—
11	$\text{NaAuCl}_4 \cdot 2\text{H}_2\text{O}$	$\text{Cs}_2\text{CO}_3$	3-Cl-pyridine	50	—
12	$\text{NaAuCl}_4 \cdot 2\text{H}_2\text{O}$	$\text{K}_3\text{PO}_4$	3-Cl-pyridine	72	12
13	$\text{NaAuCl}_4 \cdot 2\text{H}_2\text{O}$	$\text{NaOH}$	3-Cl-pyridine	—	—
14	$\text{NaAuCl}_4 \cdot 2\text{H}_2\text{O}$	—	3-Cl-pyridine	—	—

<sup>a</sup> Reactions were set in schlenk tube with **1a** (0.15 mmol),  $\text{MAuCl}_4 \cdot 2\text{H}_2\text{O}$  (0.14 mmol), and 0.5 ml 3-Cl-pyridine at 80 °C for 24 h.

<sup>b</sup> Isolated yield, the ratio of **2a** to **3a** was determined by <sup>1</sup>H NMR.

<sup>c</sup> 3-Cl-Pyridine/ $\text{H}_2\text{O}$  (5:1) as the solvent.

<sup>d</sup> Determined by <sup>1</sup>H NMR.



**Scheme 3.** ORTEP diagram (a)  $\text{IMes-AuCl}$  **2a** and (b)  $\text{IMes-AuCl}_3$  **3a**. Selected bond distances (Å) and angles (deg) 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 (deg) 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).

**Table 2**

One step to synthesize Au(I)-NHC complexes from imidazolium salts and commercially available Au(III) salts<sup>a,8</sup>

IMes·HCl (1a)	IMes-AuCl (2a)
SIMes·HCl (1b)	SIMes-AuCl (2b)
IPr·HCl (1c)	IPr-AuCl (2c)
SIPr·HCl (1d)	SIPr-AuCl (2d)

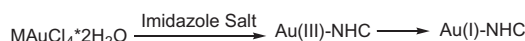
	Yield (%)
IMes-AuCl (2a)	93 <sup>b</sup>
SIMes-AuCl (2b)	72 <sup>b</sup>
	91 <sup>c</sup>
IPr-AuCl (2c)	83 <sup>b</sup>
	89 <sup>c</sup>
SIPr-AuCl (2d)	52 <sup>b</sup>
	60 <sup>c</sup>
	74 <sup>d</sup>

<sup>a</sup> Reactions were carried out using **1** (0.15 mmol), MAuCl<sub>4</sub>·2H<sub>2</sub>O (0.14 mmol), and 0.5 ml 3-Cl-pyridine in a schlenk tube, heating at 80 °C for 24 h, the yield refers to isolated yield.

<sup>b</sup> NaAuCl<sub>4</sub>·2H<sub>2</sub>O as the gold source, and Na<sub>2</sub>CO<sub>3</sub> as the base.

<sup>c</sup> KAuCl<sub>4</sub>·2H<sub>2</sub>O as the gold source, and Na<sub>2</sub>CO<sub>3</sub> as the base.

<sup>d</sup> The reaction was set at 110 °C for 24 h using KAuCl<sub>4</sub>·2H<sub>2</sub>O as the gold source, and Na<sub>2</sub>CO<sub>3</sub> as the base.



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

IMes-AuCl + IMes-AuCl <sub>3</sub>		3-Cl-Pyridine		IMes-AuCl + IMes-AuCl <sub>3</sub>	
		Na <sub>2</sub> CO <sub>3</sub> , 80 °C, 12 h			
<b>2a</b>	<b>3a</b>			<b>2a</b>	<b>3a</b>
50%	50%		100%	100%	0%

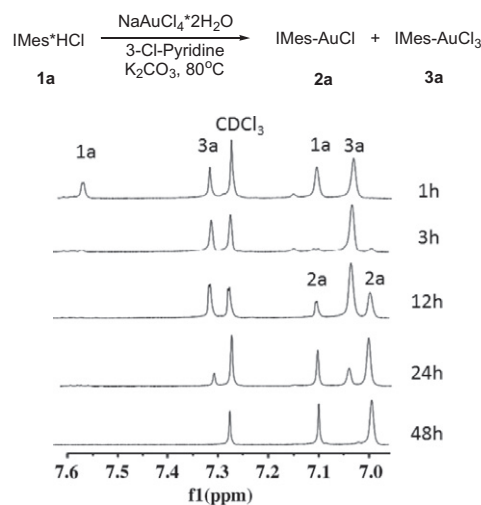
**Scheme 5.** The control reaction.

If the gold(III)-NHC was the reaction intermediate, which could be reduced further into gold(I)-NHC under the same reaction conditions. To verify this hypothesis, a control reaction was designed (Scheme 5). In the presence of 3-Cl-pyridine and Na<sub>2</sub>CO<sub>3</sub>, equal molar of IMes-AuCl (**2a**) and IMes-AuCl<sub>3</sub> (**3a**) was converted completely into IMes-AuCl (**2a**) after 12 h. These results indicated that gold(III)-NHC could be easily converted into gold(I)-NHC under the reaction conditions.

If the gold(III)-NHC is the intermediate, then it is also possible to selective prepare gold(III)-NHC under certain reaction conditions. By tuning the reaction conditions carefully and monitored the reaction results by <sup>1</sup>H NMR, the products changing's trends were obtained (Table 3). It revealed that the reaction products distributions are time-dependent. In the case of imidazolium salt **1a**, shorter reaction time gave IMes-AuCl<sub>3</sub> (**3a**) dominantly. For example, only Au(III)-NHC **3a** (77%) and the starting material **1a** (23%) was detected after 1 h reaction, no Au(I) formed (Table 3, entries 1). By prolonging the reaction time to 3 h, IMes-AuCl<sub>3</sub> (**3a**) was increased to 89%, accompanying with small amounts of unreacted imidazolium salt **1a** (4%) and IMes-AuCl (**2a**) (7%) (entry 2). After 12 h reactions, the starting material, imidazolium salt **1a**, has totally gone, with the ratio of IMes-AuCl (**2a**) and IMes-AuCl<sub>3</sub> (**3a**) being 27% and 73%, respectively. When the reaction time was prolonged to 48 h, all the starting material and gold(III)-NHC (**3a**) were converted into gold(I)-NHC **2a** (entry 5). These results further supported the above reaction pathway: gold(III)-NHC formed initially, which was then reduced to gold(I)-NHC under the reaction conditions.

**Table 3**

Time-dependent of the formation of **2a** and **3a**



Entry	Reaction time (h)	Product distribution <sup>a</sup> (%)		
		<b>1a</b>	<b>2a</b>	<b>3a</b>
1	1	23	—	77
2	3	4	7	89
3	12	—	27	73
4	24	—	71	29
5	48	—	100	—

<sup>a</sup> Product ratios were determined by <sup>1</sup>H NMR.

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<sub>2</sub>O) or using highly sensitive free NHC. The control reactions revealed that the Au(III)-NHC complexes were formed initially, which were then reduced to Au(I)-NHC under the reaction conditions. Owing to the advantages of mild reaction conditions, one step, one-pot and silver-free process, insensitiveness to the air and moisture, this reaction would be the choice for the synthesis of Au(I)-NHC complexes. Work to expand the scope and apply the method to other transitional metals is currently underway in our laboratory.

**Crystal data of 2a:** CCDC No. 824114, C<sub>21</sub>H<sub>24</sub>AuClN<sub>2</sub>, M<sub>r</sub> = 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<sup>3</sup>, Z = 8, D<sub>c</sub> = 1.698 g/cm<sup>3</sup>, T = 293(2) K. 2373 unique reflections [R(int) = 0.0575]. F(000) = 2080 Final R<sub>1</sub> [with I > 2σ(I)] = 0.0342, wR<sub>2</sub> (all data) = 0.0874. **Crystal data of 3a:** CCDC No. 824115, C<sub>21</sub>H<sub>24</sub>AuCl<sub>3</sub>N<sub>2</sub>, M<sub>r</sub> = 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) Å<sup>3</sup>, Z = 4, D<sub>c</sub> = 1.769 g/cm<sup>3</sup>, T = 293(2) K. 5214 unique reflections [R(int) = 0.0951]. F(000) = 1176, Final R<sub>1</sub> [with I > 2σ(I)] = 0.0448, wR<sub>2</sub> (all data) = 0.1127. The structures were solved by direct methods and refined on F<sup>2</sup> 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.

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## Supplementary data

Supplementary data (general procedures and spectral data) associated with this article can be found, in the online version, at [doi:10.1016/j.tetlet.2011.12.007](https://doi.org/10.1016/j.tetlet.2011.12.007).

## References and notes

- (a) Lin, J. C. Y.; Huang, R. T. W.; Lee, C. S.; Bhattacharyya, A.; Hwang, W. S.; Lin, I. J. B. *Chem. Rev.* **2009**, *109*, 3561; (b) Díez-Gonzalez, S.; Marion, N.; Nolan, S. P. *Chem. Rev.* **2009**, *109*, 3612; (c) Díaz-Requejo, M. M.; Perez, P. J. *Chem. Rev.* **2008**, *108*, 3379; (d) Patil, N. T.; Yamamoto, Y. *Chem. Rev.* **2008**, *108*, 3395; (e) Hashmi, A. S. K.; Hutchings, G. J. *Angew. Chem., Int. Ed.* **2006**, *45*, 7896; (f) Hashmi, A. S. K. *Angew. Chem., Int. Ed.* **2005**, *44*, 6990.
- (a) Li, Z.; Brouwer, C.; He, C. *Chem. Rev.* **2008**, *108*, 3239; (b) Arcadi, A. *Chem. Rev.* **2008**, *108*, 3266; (c) Jimenez-Nunez, E.; Echavarren, A. M. *Chem. Rev.* **2008**, *108*, 3326; (d) Gorin, D. J.; Sherry, B. D.; Toste, F. D. *Chem. Rev.* **2008**, *108*, 3351; (e) Hashmi, A. S. K.; Rudolph, M. *Chem. Soc. Rev.* **2008**, *37*, 1766.
- (a) Nolan, S. P. *Acc. Chem. Res.* **2011**, *44*, 91; (b) Marion, N.; Nolan, S. P. *Chem. Soc. Rev.* **2008**, *37*, 1776; (c) Raubenheimer, H. G.; Cronje, S. *Chem. Soc. Rev.* **2008**, *37*, 1998.
- (a) Wang, H. M. J.; Lin, I. J. B. *Organometallics* **1998**, *17*, 972; (b) de Fremont, P.; Scott, N. M.; Stevens, E. D.; Ramnial, T.; Lightbody, O. C.; Macdonald, C. L. B.; Clyburne, J. A. C.; Abernethy, C. D.; Nolan, S. P. *Organometallics* **2005**, *24*, 6301; (c) de Fremont, P.; Scott, N. M.; Stevens, E. D.; Nolan, S. P. *Organometallics* **2005**, *24*, 2411; (d) Nieto-Oberhuber, C.; Lopez, S.; Echavarren, A. M. *J. Am. Chem. Soc.* **2005**, *127*, 6178.
- Schmidbaur, H. *Gold, Progress in Chemistry, Biochemistry and Technology*; Wiley: West Sussex, England, 1999. p 358.
- Ahmad, S.; Isab, A. A.; Perzanowski, H. P.; Hussain, M. S.; Akhtar, M. N. *Transition Met. Chem.* **2002**, *27*, 177.
- (a) Samantaray, M. K.; Dash, C.; Shaikh, M. M.; Pang, K.; Butcher, R. J.; Ghosh, P. *Inorg. Chem.* **2011**, *50*, 1840; (b) de Fremont, P.; Singh, R.; Stevens, E. D.; Petersen, J. L.; Nolan, S. P. *Organometallics* **2007**, *26*, 1376; (c) Gaillard, S.; Bantreil, X.; Slawin, A. W.; Nolan, S. P. *Dalton Trans.* **2009**, 6967.
- Representative experimental procedure for the synthesis of NHC–AuCl: Potassium chloroaurate dihydrate (58.1 mg, 0.14 mmol) or sodium chloroaurate dehydrate (55.7 mg, 0.14 mmol) and the imidazol(idin)ium chloride (0.15 mmol) and sodium carbonate (72.1 mg, 0.68 mmol) were introduced in a schlenk equipped with a magnetic stirring bar. The schlenk was then added 3-chloropyridine (0.5 ml), the reaction mixture was stirred at 80 °C for 24 h. The schlenk was allowed to cool to room temperature, 1 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, after filtered and dried, affording pure (NHC)AuCl. For more detail information, please see electronic [Supplementary data](#).