

# Synthesis of cationic gold(III) complexes using iodine(III)

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## Abstract

We report the synthesis and characterization of cationic Au(III) complexes supported by nitrogen-based ligands. The synthesis is achieved by reacting Au(I) complexes  $[\text{Au}(\text{N-Me-imidazole})_2]^+$  and  $[\text{Au}(\text{pyridine})(\text{NHC})]^+$  with iodine(III) reagents  $\text{PhI}(\text{OTf})(\text{OAc})$  and  $[\text{PhI}(\text{pyridine})_2]^{2+}$  yielding a series of cationic gold(III) complexes. In contrast, reactions of phosphine ligated gold(I) complexes with iodine(III) reagents results in the oxidation of the phosphine ligand.

Gold I/III redox catalysis has attracted much attention recently in organic synthesis,[1] however, oxidative addition reactions are not readily accessible at Au(I) due to the high oxidation potential of Au(I).[2, 3] For catalysis to occur via Au(I)/Au(III) redox forcing conditions are required which can be achieved using external oxidants such as trivalent iodine reagents.[4-10] In one report, Blank and de Frémont have displayed the use of  $\text{PhICl}_2$  in generating (NHC)-Au(III) complexes. However, attempts in generating tricationic Au(III) complexes bound by only neutral ligands by exchanging the chlorides with pyridines using silver salts were unsuccessful (Scheme 1).[11]



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materials bear a chloride ligand as did **7**. Reactions involving homoleptic complexes (i.e.,  $[\text{dppe}]_2\text{Rh}(\text{I})$ ) without halides went much more cleanly.[13]

Direct reaction of  $\text{PPh}_3$  with **5R** resulted in oxidation of the phosphine, generating dication **18**, previously reported by Burford from halide abstraction/coordination reactions at chlorophosphonium cations.[14, 15]

Based on these results, we hypothesized that scrambling is induced by the presence of a halide substituent, and have investigated the reactions of selected phosphine or NHC containing Au(I) complexes as well as N-bound Au(I) complexes **11-14** with **5R** (Figure 1). The results show that oxidized phosphine and/or scrambling were observed in all phosphine-containing Au(I) complexes reactions. In the reaction of N-bound Au(I) complexes with **5R**, cationic Au(III) compounds were generated in high yields and no scrambling was observed. For Au(I)-NHC complexes without halides we are able to generate previously inaccessible mono-NHC-trispyridine trications.

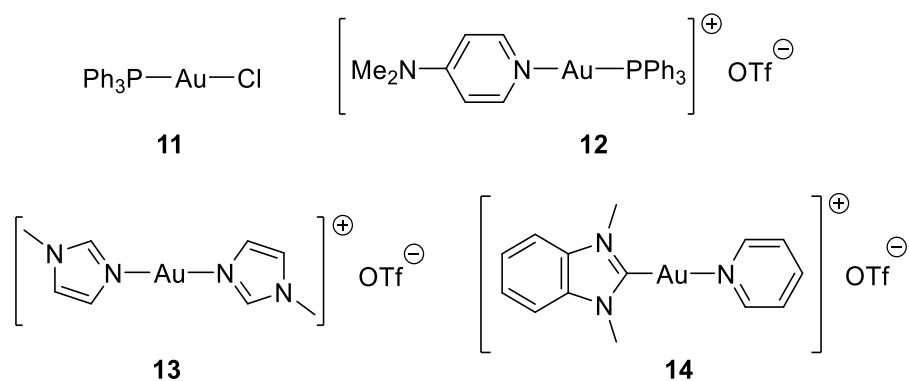
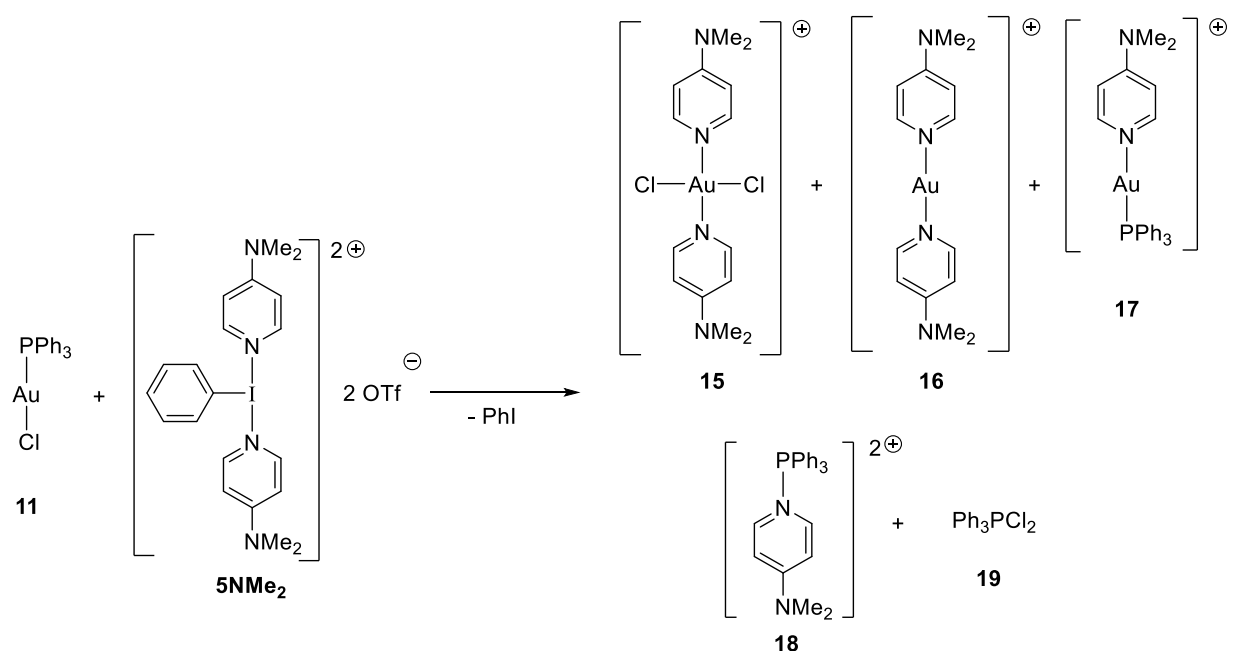


Figure 1. Au(I) complexes used in this study.

## 2. Results and discussion

### 2.1. Reactions of phosphine gold complexes.

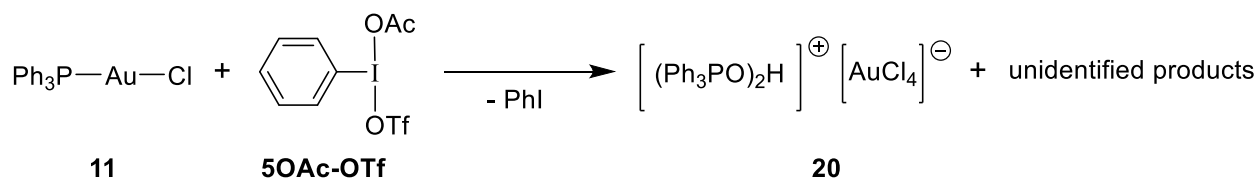
Reaction of **11** with **5NMe<sub>2</sub>** in CD<sub>3</sub>CN resulted in a color change to orange within 10 minutes. The <sup>1</sup>H NMR spectrum of the reaction mixture indicated that there was a complex mixture of products present. The <sup>31</sup>P NMR spectrum of the reaction mixture gave 4 peaks (65.6, 57.6, 33.0 and 29.9 ppm). The peaks at 65.6 and 57.6 ppm are consistent with the reported compounds **18** and **19** respectively.[14, 16] The peaks at 33.0 and 29.9 are consistent with the gold compounds **11** and **17** respectively.[17, 18] Positive mode ESI-MS detection of a CH<sub>3</sub>CN solution of the reaction mixture gave fragments that could be identified at [m/z]<sup>+</sup> = 510.4 consistent with **15** and [m/z]<sup>+</sup> = 440.8 consistent with **16** (Scheme 4). The outcome of this reaction showed similar scrambling pattern to that observed in reaction of **7** with **5NMe<sub>2</sub>** with the addition of products **18** and **19** apparently arising from reductive elimination reactions.



Scheme 4. Reaction of **11** with **5NMe<sub>2</sub>** outcome as identified by mass spectrometry and <sup>31</sup>P NMR.

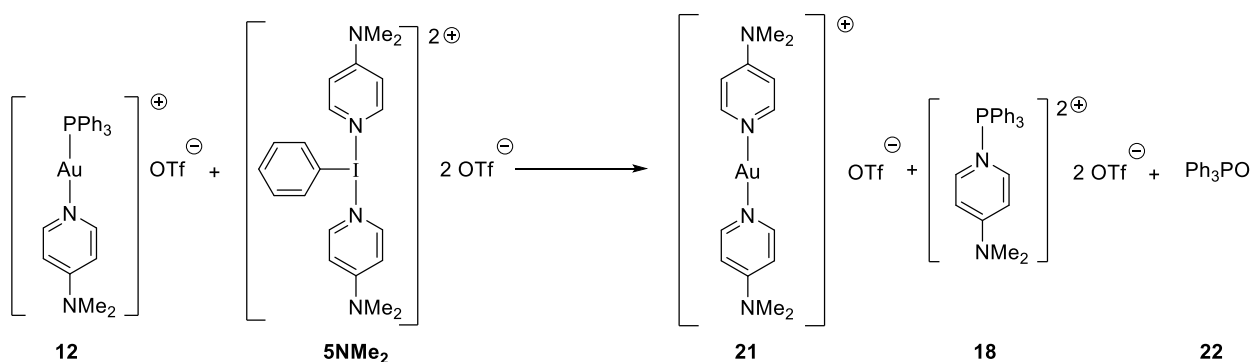
The reaction of **11** with **5OAc-OTf** in a 1:1 ratio in CDCl<sub>3</sub> resulted in a color change to yellow instantly (Scheme 5). The <sup>1</sup>H NMR spectrum of the mixture indicated the presence of iodobenzene and one other species. The <sup>31</sup>P NMR of the solution had one singlet at 52.1 ppm. Searching the literature for potential oxidized phosphine products revealed that [Ph<sub>3</sub>P-OTf][OTf] has been reported to give an identical chemical shift.[14] The Ph<sub>3</sub>PO was not detected in the <sup>31</sup>P NMR of the crude reaction, but it can be rationalized by the reported behavior of [Ph<sub>3</sub>P-OTf][OTf] where an equilibrium between [Ph<sub>3</sub>P-OTf][OTf] and Ph<sub>3</sub>PO + triflic anhydride was observed.[19, 20] The positive ESI-MS detection of the mixture contained signal at [m/z]<sup>+</sup> = 556.1 corresponding to [(Ph<sub>3</sub>PO)<sub>2</sub>H]<sup>+</sup>. X-Ray diffraction studies were done on single crystals obtained from vapor diffusion of Et<sub>2</sub>O into concentrated CH<sub>2</sub>Cl<sub>2</sub> solution revealed the crystal to be compound **20** which consists of

two  $\text{Ph}_3\text{PO}$  that are bridged with a proton and  $[\text{AuCl}_4]^-$ . This unproductive byproduct was previously reported as  $[\text{FeBr}_4]^-$ ,  $[\text{ICl}_4]^-$  and  $[\text{AuBr}_4]^-$  and  $[\text{AuCl}_4]^-$  salts.[21-25]



Scheme 5. Reaction of **11** with **5OAc-OTf** outcome as identified by mass spectrometry, X-ray diffraction and  $^{31}\text{P}$  NMR.

Treatment of compound **12** with **5NMe<sub>2</sub>** resulted in a color change to orange within 10 minutes. The  $^{31}\text{P}$  NMR spectrum of the mixture contained signals at 57.6 and 26.6 ppm which are consistent with compounds **18** and **22** respectively (Scheme 6).[11, 14] The starting material (compound **12**) was also detected in the  $^{31}\text{P}$  NMR at 29.7 ppm and in the cationic ESI mass spectrum of the reaction mixture ( $[\text{m/z}]^+ 580.0$ ). The fragment in the ESI mass spectrum at  $[\text{m/z}]^+ = 440.8$  is consistent with **21**.



Scheme 6. Reaction of **12** with **5NMe<sub>2</sub>** outcome as identified by mass spectrometry and  $^{31}\text{P}$  NMR.

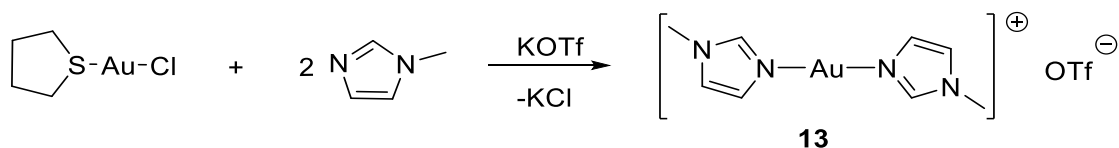
The reaction of **12** with **5OAc-OTf** resulted in color change to yellow instantly followed by the formation of a black solid. The  $^{31}\text{P}$  NMR of the reaction mixture gave signals at 52.1 ppm representing  $[\text{Ph}_3\text{P-OTf}][\text{OTf}]$  which is in equilibrium with  $\text{Ph}_3\text{PO}$  and triflic anhydride. Positive mode ESI-MS detection of a  $\text{CH}_3\text{CN}$  solution of the reaction mixture gave fragments that could be identified at  $[m/z]^+ = 556.2$  consistent with  $[(\text{PPh}_3\text{O})_2\text{H}]^+$  and  $[m/z]^+ = 499.4$  consistent with  $[\text{Au}(\text{PPh}_3)(\text{CH}_3\text{CN})]^+$ .

It is evident that the reactions of phosphine-containing gold(I) complexes with the selected I(III) resulted in the oxidation of  $\text{PPh}_3$  and no phosphine-Au(III) complexes were isolated. Reaction of **12** with  $\text{PhICl}_2$  (**5Cl**) was not attempted as this reaction (using pyridine-Au(I)- $\text{PPh}_3$  instead of (4-DMAP)-Au(I)- $\text{PPh}_3$  as starting material) was previously reported and gave similar scrambling patterns to what has been observed in our reactions.[11]

## 2.1. Reactions of N-imidazole Au(I) complexes

The Au(I) starting complex **13** was achieved *via* adapting the synthetic protocol of Lin[26] and using N-methylimidazole as the ligand in place of 4-DMAP (Scheme 7). The same cation has previously been reported as an  $[\text{AuCl}_2]^-$  salt.[27] Compound **13** has a linear structure with normal Au-N bond lengths and they are lined parallel with a Au-Au contact of about 3.26 Å (Figure 2).





Scheme 7. Synthesis of compound **13**

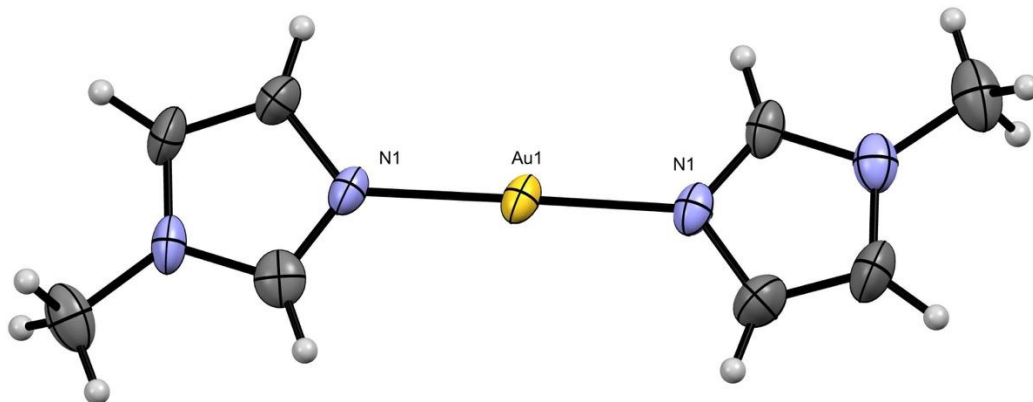
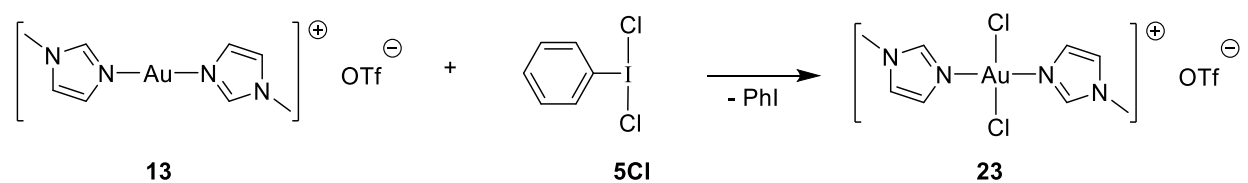


Figure 2. Solid-state structure of **13**. Thermal ellipsoids are drawn at the 50% probability level. Anions and solvate were omitted for clarity (OTf, CH<sub>3</sub>CN). Selected bond distances (Å) Au1-N1 2.000(7).

Reaction of **13** with **5Cl** in CH<sub>2</sub>Cl<sub>2</sub> resulted in the formation of a yellow solid. The solid was filtered and washed with CH<sub>2</sub>Cl<sub>2</sub>. <sup>1</sup>H NMR analysis of the solid in CD<sub>3</sub>CN gave a set of resonances consistent with a single N-methylimidazole containing product (Scheme 8). Mass spectrometry in CH<sub>3</sub>CN showed signals arising from compound **23** which was further confirmed by X-Ray diffraction studies on single crystals obtained from vapor diffusion of Et<sub>2</sub>O into concentrated CH<sub>3</sub>CN solution of the isolated solid (Figure 3).



Scheme 8. Synthesis of compound **23**.

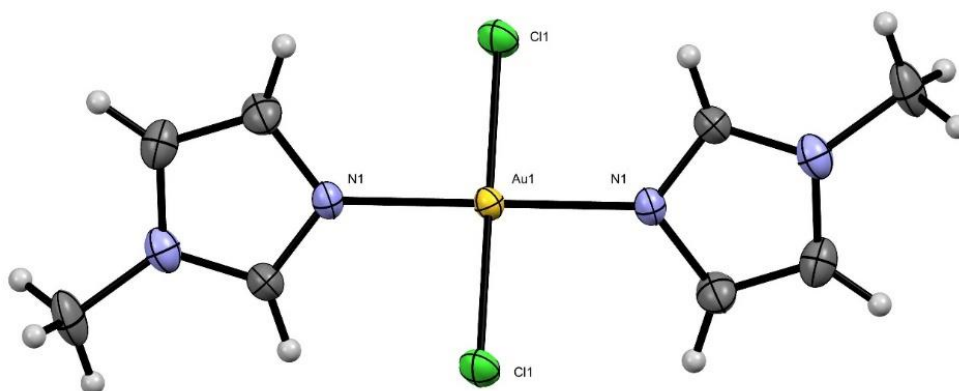
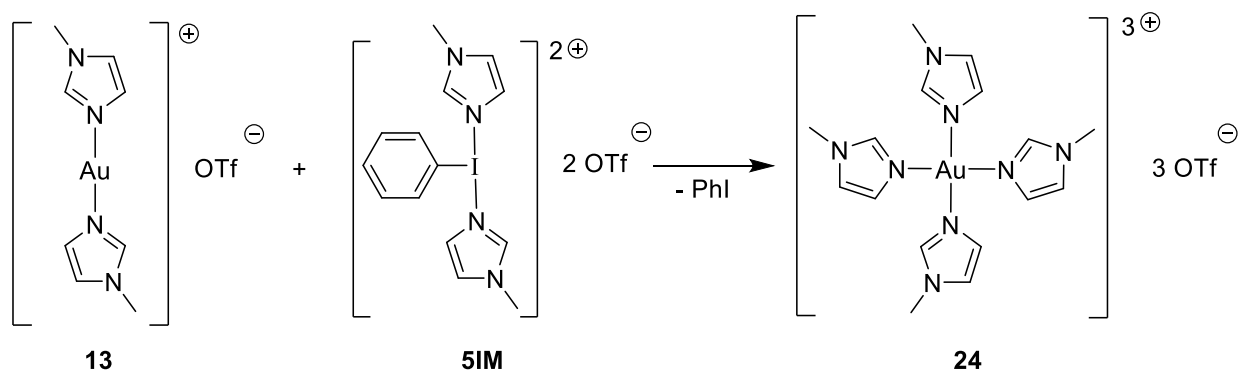


Figure 3. Solid-state structure of **23**. Thermal ellipsoids are drawn at the 50% probability level. Anions and solvate were omitted for clarity (OTf, CH<sub>3</sub>CN). Selected bond distances (Å) Au1-N1 2.007(6), Au1-Cl1 2.277(17).

Reaction of **13** with **5IM** in CH<sub>3</sub>CN (Scheme 9) resulted in a color change to yellow within 5 minutes. The solvent was removed under reduced pressure to give a pale yellow solid. The solid was then recrystallized from CH<sub>3</sub>CN/Et<sub>2</sub>O.



Scheme 9. Synthesis of compound **24**.

<sup>1</sup>H NMR spectroscopy was consistent with a single compound containing N-methylimidazole. The signal at  $[m/z]^+ = 823.1$  in the positive ESI-MS spectrum of the mixture corresponds to  $[\text{Au}(\text{N-methylimidazole})_4 2\text{OTf}]^+$ . Single crystals were grown from a CH<sub>3</sub>CN solution of the compound via slow vapor diffusion of Et<sub>2</sub>O and subsequent X-ray diffraction studies confirmed homoleptic complex **24** (Figure 4), which is isolated in 79% yield. This compound is the second example of a homoleptic N-imidazole containing Au(III) trication. The first reported example incorporated an extended Au-ligand framework for the synthesis of Au nanoparticles without structural or spectroscopic characterization.[28]

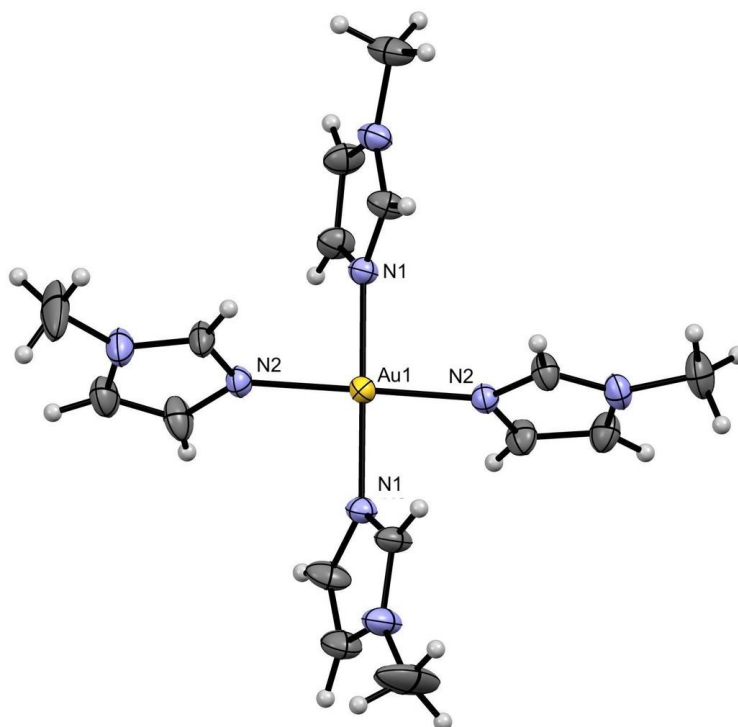
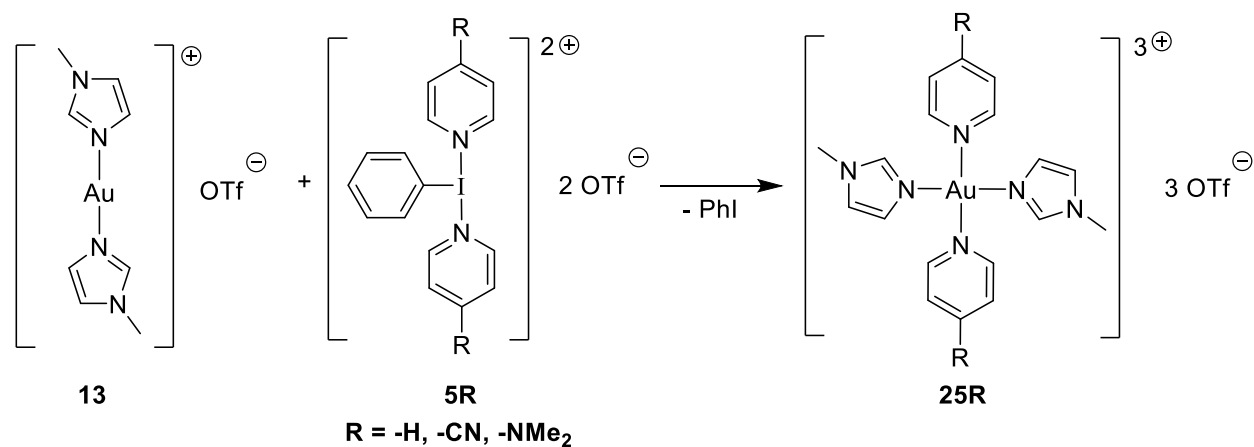


Figure 4. Solid-state structure of **24**. Thermal ellipsoids are drawn at the 50% probability level. Anions and solvate were omitted for clarity (OTf, CH<sub>3</sub>CN). Selected bond distances (Å) Au1-N1 1.996(3), Au1-N2 1.999(3).

Using I(III) oxidant **5R** resulted in the corresponding pseudo-homoleptic compounds **25H**, **25CN** and **25NMe<sub>2</sub>** respectively in good yields (Scheme 10). In previous work we reported the synthesis and the use of **25CN** in generating difluorogold(III) complexes but the crystal structure was not reported.[29] The solid state structures of compounds **25H** and **25CN** are depicted in Figures 5 and 6. Unfortunately no crystals of diffraction quality could be obtained for compound **25NMe<sub>2</sub>**.

The reaction of **5OAc-OTf** with **13** in CHCl<sub>3</sub> resulted in a decomposition of the Au complex which was indicated by the formation of black solid.



Scheme 10. Synthesis of Au(III) trications **25R**.

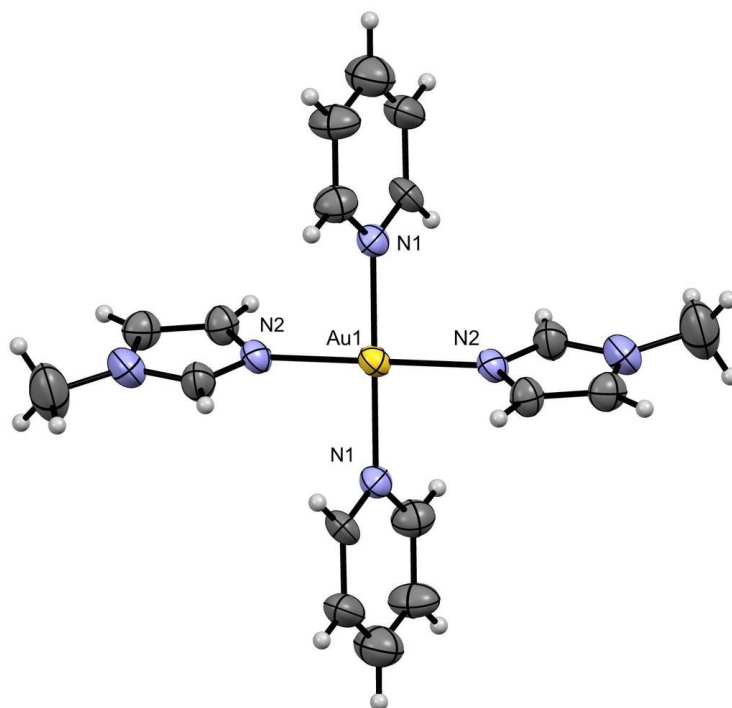


Figure 5. Solid-state structure of **25H**. Thermal ellipsoids are drawn at the 50% probability level. Anions and solvate were omitted for clarity (OTf, CH<sub>3</sub>CN). Selected bond distances (Å) Au1-N1 2.016(5), Au1-N2 2.009(4).

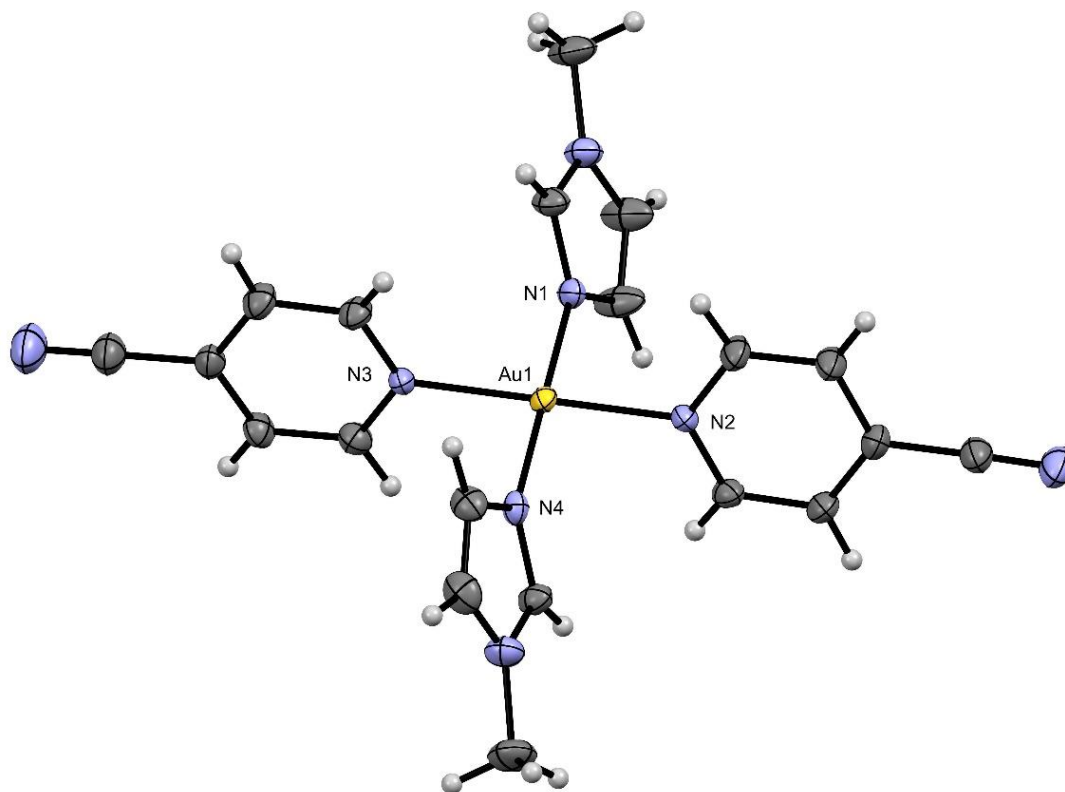
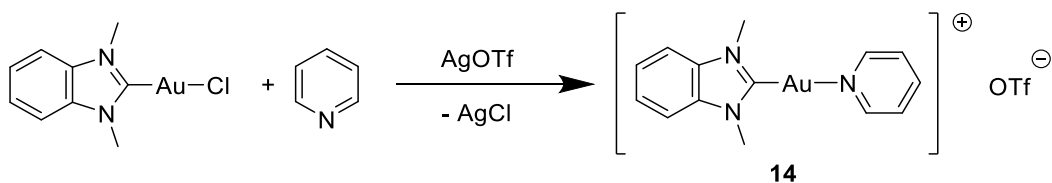


Figure 6. Solid-state structure of **25CN**. Thermal ellipsoids are drawn at the 50% probability level. Anions and solvate were omitted for clarity (OTf, CH<sub>3</sub>CN). Selected bond distances (Å) Au1-N1 2.006(4), Au1-N2 2.035(4), Au1-N3 2.024(4), Au1-N4 1.991(4).

The starting complex **14** was synthesized using the synthetic protocol of de Frémont [11] and using 1,3-Dimethylbenzimidazol-2-ylidene as the ligand (Scheme 11). The solid state structure of **14** is shown in Figure 7.



Scheme 11. Synthesis of compound **14**.

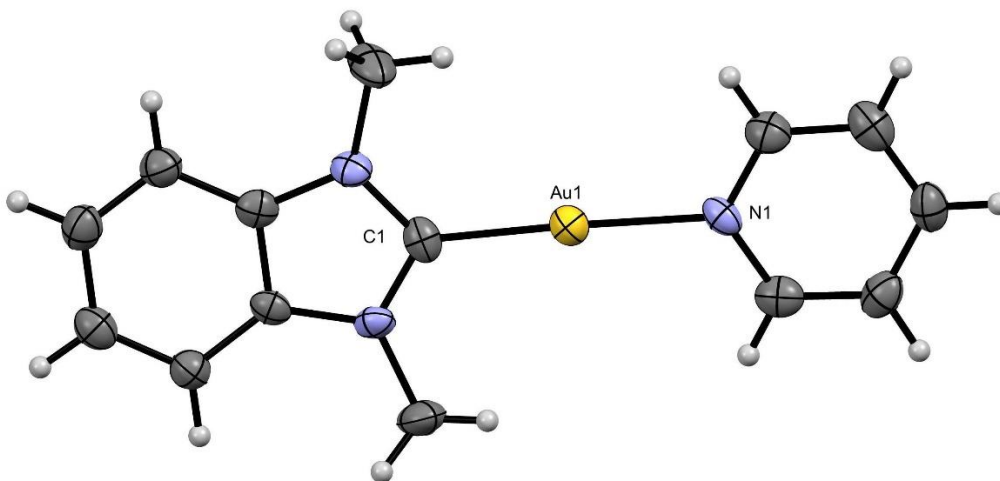
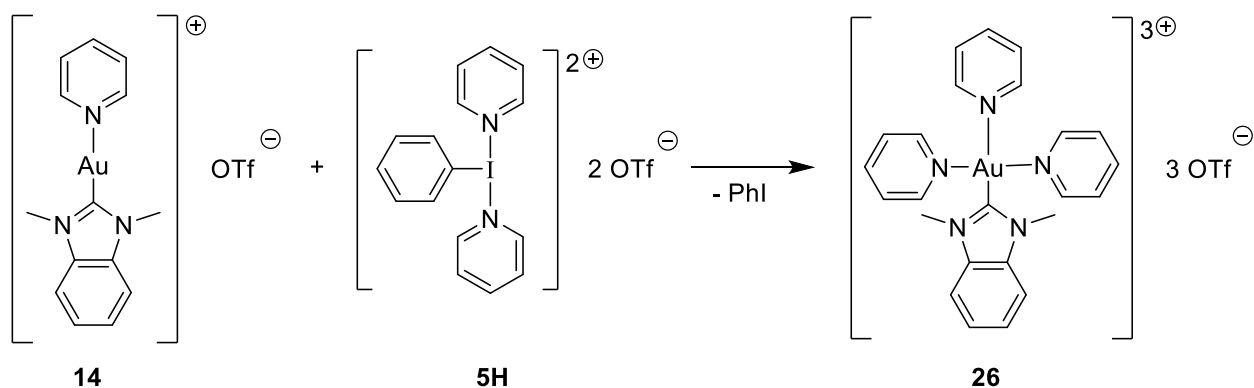


Figure 7. Solid-state structure of **14**. Thermal ellipsoids are drawn at the 50% probability level. Anions and solvate were omitted for clarity (OTf, CH<sub>3</sub>CN). Selected bond distances (Å) Au1-N1 2.052(5), Au1-C1 1.975(7).

Reaction of **14** with PhICl<sub>2</sub> was not attempted as similar reactions were previously reported on Au(I) compounds with different NHC ligands.[11] Treatment of compound **14** with **5H** in CH<sub>3</sub>CN at room temperature for 30 minutes followed by workup resulted in the isolation of a yellow solid. The <sup>1</sup>H NMR spectrum of the isolated solid was consistent with a single compound containing one 1,3-Dimethylbenzimidazol-2-ylidene and three pyridine ligands (Scheme 12). The positive ESI-MS detection of the mixture indicated the presence of **26** at [m/z]<sup>+</sup> = 877.8 as monocationic [Au(NHC)(pyridine)<sub>3</sub> 2OTf]<sup>+</sup>.



Scheme 12. Synthesis of compound **26**.

X-Ray diffraction studies were done on single crystals obtained from vapor diffusion of Et<sub>2</sub>O into concentrated CH<sub>3</sub>CN solution of the isolated solid confirmed the compound to be **26** (Figure 8).

Reaction of **14** with **5OAc-OTf** in CDCl<sub>3</sub> resulted in the formation of a black solid due to decomposition of Au complex.

The synthesis of Au(III) cationic complexes (**23-26**) was achieved in good yield (68%-85%) and purity. Prior attempts to generate tricationic Au(III) compounds using silver salts to replace two chlorides from Au(III) compounds with pyridine ligands resulted in complex decomposition demonstrating the ability of I(III) reagents in cleanly oxidizing N-bound Au(I) complexes.[11]



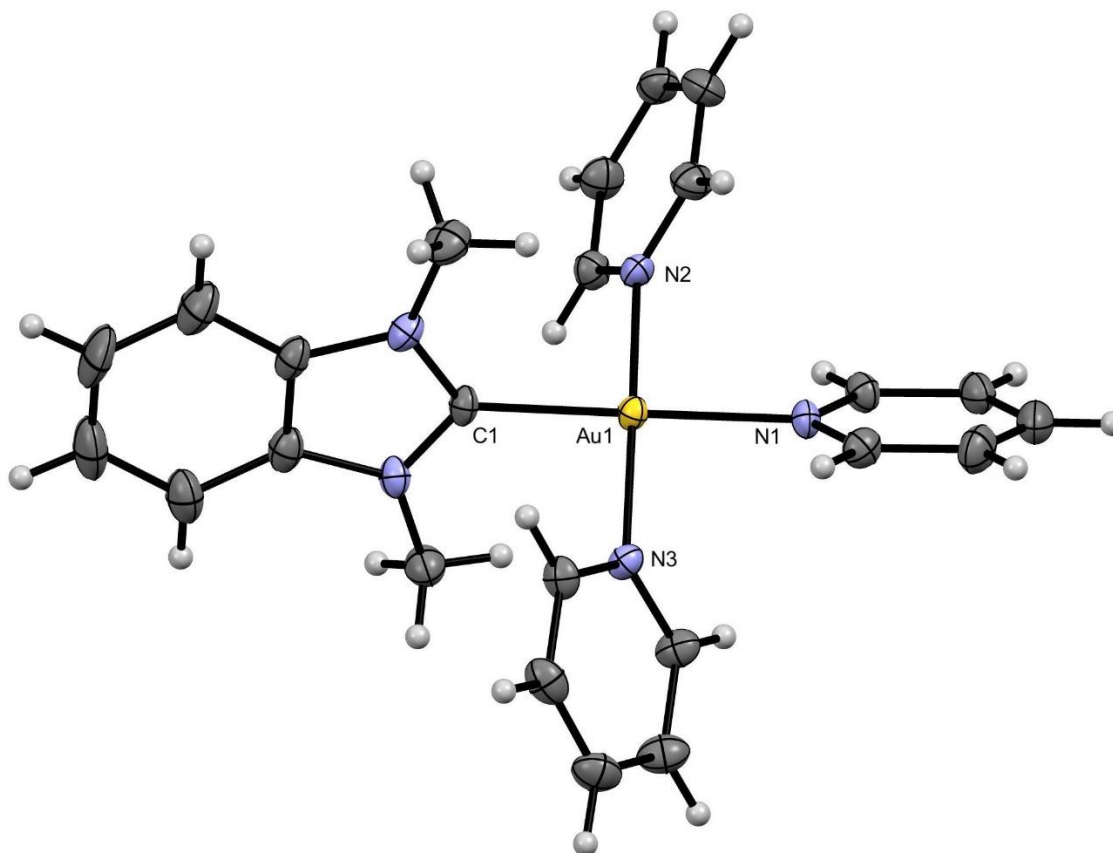


Figure 8. Solid-state structure of **26**. Thermal ellipsoids are drawn at the 50% probability level. Anions and solvate were omitted for clarity (OTf, CH<sub>3</sub>CN). Selected bond distances (Å) Au1-N1 2.085(3), Au1-N2 2.025(3), Au1-N3 2.021(3), Au1-C1 2.032(3).

### 3. Conclusion

We had previously shown that Au(I) starting materials of the type NHC-Au-Cl when reacted with I(III) oxidants [PhI(pyr)]<sup>2+</sup> results in complex mixtures arising from chloride scrambling. Here it was shown the eliminating the presence of chloride and replacing it with a neutral pyridine ligand suppresses the scrambling reactions. With Ph<sub>3</sub>P-Au-Cl starting complexes, scrambling and phosphine oxidation processes result. Substituting the halide with a pyridine ligand still resulted in oxidation of the phosphine in reactions

with I(III), indicating phosphine ligands are not ideal for exploring this class of reaction. Imidazole ligated Au(I) starting complexes were shown to undergo clean oxidations with both  $[\text{PhI}(\text{pyr})_2]^{2+}$  and  $\text{PhICl}_2$  oxidants.

#### 4. Experimental procedures

Solvents were obtained from Caledon Laboratories and dried using an Innovative Technologies Solvent Purification System with dual columns packed with alumina. The dried solvents were stored under an  $\text{N}_2$  atmosphere over 3 Å molecular sieves in the glovebox. Solvents used for NMR spectroscopy were purchased from Cambridge Isotopes or Sigma-Aldrich and were dried with  $\text{CaH}_2$  and stirred for 2 days and distilled and then stored in the glove box over 3 Å molecular sieves. Compounds **11**,<sup>[30]</sup> **12**,<sup>[18]</sup> **13**,<sup>[26]</sup> **14**,<sup>[11]</sup> **5CI**<sup>[31]</sup> and **5R**<sup>[32]</sup> were synthesised via literature procedures. **5OAc-OTf** was prepared in situ by treating one equivalent of diacetoxyiodobenzene with two equivalent of TMS-triflate in  $\text{CHCl}_3$ . Gold powder was purchased from Precious Metals Online. All other reagents were purchased from Alfa Aesar or Sigma Aldrich and used as received.

##### 4.1. Reaction of **11** with **5NMe<sub>2</sub>**.

A solution of **5NMe<sub>2</sub>** (82 mg, 0.11 mmol) in 3 mL  $\text{CD}_3\text{CN}$  was added drop wise to **11** (50 mg, 0.10 mmol) in 3 mL  $\text{CD}_3\text{CN}$ . The mixture was stirred for 3 hours resulting in a color change to orange. Aliquot was removed for NMR and mass spectrometry analysis.  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 65.6 (s), 57.6 (s), 33.0 (s), 29.9 (s). ESI-MS  $[\text{M}]^{n+}$ :  $m/z$  273.8  $[\text{Au}(\text{CH}_3\text{CN})\text{Cl}]^+$ , 440.8  $[\text{Au}(4\text{-dmap})_2]^+$ , 510.4  $[\text{Au}(4\text{-dmap})_2\text{Cl}_2]^+$ . See supporting

information for  $^1\text{H}$  NMR.

#### 4.2. Reaction of **11** with 5OAc-OTf.

A mixture of diacetoxyiodobenzene (21 mg, 0.065 mmol) and TMS-OTf (24  $\mu\text{L}$ , 0.13 mmol) in 2 mL  $\text{CDCl}_3$  was added drop wise to a solution of **11** (30 mg, 0.061 mmol) in 2 mL  $\text{CDCl}_3$ . The mixture was stirred for 30 minutes resulting in a yellow mixture and a black solid. The solid was filtered and the filtrate was collected. Solvent removed under reduced pressure to give a yellow solid which was washed with  $\text{Et}_2\text{O}$ .  $^{31}\text{P}$  NMR (162 MHz,  $\text{CD}_3\text{CN}$ )  $\delta$  (ppm): 52.1 (s). ESI-MS  $[\text{M}]^{n+}$ :  $m/z$  273.8  $[\text{Au}(\text{CH}_3\text{CN})\text{Cl}]^+$ , 556.1  $[(\text{Ph}_3\text{PO})_2\text{H}]^+$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  (ppm) = 7.91-7.87 (m), 7.78-7.70 (m).

#### 4.3. Reaction of **12** with 5NMe<sub>2</sub>.

A solution of 5NMe<sub>2</sub> (52 mg, 0.070 mmol) in 2 mL  $\text{CH}_3\text{CN}$  was added to a solution of **12** (50 mg, 0.068 mmol) in 2 mL  $\text{CH}_3\text{CN}$  drop wise. The mixture was stirred for 3 hours resulting in an orange solution. Solvent removed under reduced pressure and the resulting orange solid was washed with  $\text{Et}_2\text{O}$ .  $^{31}\text{P}$  NMR (162 MHz,  $\text{CD}_3\text{CN}$ )  $\delta$  (ppm): 57.6 (s), 29.7 (s), 26.6 (s). ESI-MS  $[\text{M}]^{n+}$ :  $m/z$  395.0  $[\text{Ph}_3\text{P}]^{2+}[\text{Tf}]^-$ , 440.8  $[\text{Au}(4\text{-dmap})_2]^+$ , 499.4  $[\text{Au}(\text{PPh}_3)(\text{CH}_3\text{CN})]^+$ , 580.0  $[\text{Au}(\text{PPh}_3)(4\text{-dmap})]^+$ , 736.2  $[\text{Au}(\text{PPh}_3)(\text{Ph}_3\text{PO})]^+$ . See supporting information for  $^1\text{H}$  NMR.

#### 4.4. Reaction of **12** with 5OAc-OTf.

A mixture of diacetoxyiodobenzene (21 mg, 0.065 mmol) and TMS-OTf (24  $\mu\text{L}$ , 0.13 mmol) in 2 mL  $\text{CHCl}_3$  was added drop wise to **12** (45 mg, 0.062 mmol) in 2 mL  $\text{CHCl}_3$  and stirred for 30 minutes. The resulting black solid was filtered, and aliquot of the filtrate was

removed for NMR and mass spectrometry analysis.  $^{31}\text{P}$  NMR (162 MHz,  $\text{CHCl}_3$ )  $\delta$  (ppm): 52.1 (s), 27.8 (s). ESI-MS  $[\text{M}]^+$ :  $m/z$  556.2  $[(\text{PPh}_3\text{O})_2\text{H}]^+$ , 499.4  $[\text{Au}(\text{PPh}_3)(\text{CH}_3\text{CN})]^+$ .

#### 4.5. Synthesis of 13.

N-methylimidazole (175  $\mu\text{L}$ , 2.20 mmol) was added to a dichloromethane solution (20 mL) containing  $\text{tht-AuCl}$  (350 mg, 1.09 mmol) and KOTf (210 mg, 1.12 mmol). The mixture was stirred for 24 hours in the dark. The solvent was removed under vacuum to give a light yellow solid. The solid was washed with  $\text{Et}_2\text{O}$  and recrystallized from  $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$  to give a white solid (457 mg, 82%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 8.26 (s, 2H), 7.13 (s, 2H), 7.05 (s, 2H), 3.84 (s, 6H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 141.00, 129.44, 121.71, 35.23. ESI-MS  $[\text{M}]^+$ :  $m/z$  361  $[\text{Au}(\text{N-methylimidazole})_2]^+$ .

#### 4.6. Synthesis of 23.

A solution of **5Cl** (27 mg, 0.098 mmol) in 2 mL  $\text{CH}_2\text{Cl}_2$  was added drop wise to a solution of **13** (50 mg, 0.098 mmol) in 2 mL  $\text{CH}_2\text{Cl}_2$ . The mixture was then stirred for 30 minutes resulting in a yellow solid. The solid was filtered, washed with  $\text{CH}_2\text{Cl}_2$  (3 X 3 mL) and dried *in vacuo* (49 mg, 85% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  (ppm) = 8.30 (s, 2H), 7.39 (s, 2H), 7.35 (s, 2H), 3.86 (s, 6H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  (ppm) = 139.69, 127.74, 123.89, 36.54. ESI-MS  $[\text{M}]^+$ :  $m/z$  361.0  $[\text{Au}(\text{N-methylimidazole})_2]^+$ , 395.0  $[\text{Au}(\text{N-methylimidazole})_2\text{Cl}]^+$ , 431.0  $[\text{Au}(\text{N-methylimidazole})_2\text{Cl}_2]^+$ .

#### 4.7. Synthesis of 24.

A solution of **5IM** (66 mg, 0.098 mmol) in 2 mL CH<sub>3</sub>CN was added drop wise to a solution of **13** (50 mg, 0.098 mmol) in 2 mL CH<sub>3</sub>CN. The mixture was stirred for 30 minutes resulting in a yellow solution. Solvent was reduced to half *in vacuo* followed by the addition of 5 mL of Et<sub>2</sub>O to afford a yellow solid. The solid was then washed with Et<sub>2</sub>O (3 X 3 mL) and dried *in vacuo* (76 mg, 70% yield). <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN): δ (ppm) = 8.20 (s, 4H), 7.32 (s, 4H), 7.20 (s, 4H), 3.80 (s, 12H). <sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>CN): δ (ppm) = 139.50, 126.53, 124.76, 36.66. ESI-MS [M]<sup>+</sup>: *m/z* 361.1 [Au(N-methylimidazole)<sub>2</sub>]<sup>+</sup>, 823.1 [Au(N-methylimidazole)<sub>4</sub>]<sup>3+</sup> [OTf]<sub>2</sub><sup>-</sup>.

#### 4.8. Synthesis of 25NMe<sub>2</sub>.

A solution of **5NMe<sub>2</sub>** (74 mg, 0.098 mmol) in 2 mL CH<sub>3</sub>CN was added drop wise to a solution of **13** (50 mg, 0.098 mmol) in 2 mL CH<sub>3</sub>CN and stirred for 30 minutes. A color change from white to orange was observed. Solvent was reduced to half *in vacuo* followed by the addition of 5 mL of Et<sub>2</sub>O to afford a yellow solid. The solid was then washed with Et<sub>2</sub>O (3 X 3 mL) and dried *in vacuo* (78 mg, 76% yield). <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN): δ (ppm) = 8.24 (s, 2H), 7.95 (d, 4H, *J* = 8 Hz), 7.33 (s, 2H), 7.22 (s, 2H), 6.71 (d, 4H, *J* = 8 Hz), 3.79 (s, 6H), 3.11 (s, 12H). <sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>CN): δ (ppm) = 157.02, 147.10, 139.46, 126.26, 124.98, 110.25, 40.24, 36.70. ESI-MS [M]<sup>+</sup>: *m/z* 361.1 [Au(N-methylimidazole)<sub>2</sub>]<sup>+</sup>, 401.1 [Au(N-methylimidazole)(4-dmap)]<sup>+</sup>, 441.1 [Au(4-dmap)<sub>2</sub>]<sup>+</sup>, 902.9 [Au(N-methylimidazole)<sub>2</sub>(4-dmap)<sub>2</sub>]<sup>+</sup>[OTf]<sub>2</sub><sup>-</sup>.

#### 4.9. Synthesis of 25H.

A solution of **5H** (65 mg, 0.098 mmol) in 2 mL CH<sub>3</sub>CN was added drop wise to a solution of **13** ( 50 mg, 0.098 mmol) in 2 mL CH<sub>3</sub>CN and stirred for 30 minutes. A color change from white to yellow was observed. Solvent was reduced to half *in vacuo* followed by the addition of 5 mL of Et<sub>2</sub>O to afford a yellow solid. The solid was then washed with Et<sub>2</sub>O (3 X 3 mL) and dried *in vacuo* (68 mg, 72% yield). <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN): δ (ppm) = 8.77 (d, 4H, *J* = 8 Hz), 8.36-8.31 (m, 4H), 7.83 (t, 4H, *J* = 8 Hz), 7.3 (s, 4H), 3.75 (s, 6H). <sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>CN): δ (ppm) = 150.75, 146.29, 139.56, 130.62, 125.92, 125.40, 36.76. ESI-MS [M]<sup>+</sup>: *m/z* 358.1 [Au(N-methylimidazole)(pyridine)]<sup>+</sup>, 361.1 [Au(N-methylimidazole)<sub>2</sub>]<sup>+</sup>, 816.5 [Au(N-methylimidazole)<sub>2</sub>(pyridine)<sub>2</sub>]<sup>3+</sup>[OTf]<sup>-2</sup>.

#### 4.10. Synthesis of **25CN**

A solution of **5CN** (278 mg, 0.392 mmol) in CH<sub>3</sub>CN (5 mL) was added drop wise to a solution of **13** (200 mg, 0.392 mmol) in CH<sub>3</sub>CN (5 mL). The mixture was then stirred for 10 minutes giving a yellow solution. The solvent was removed under reduced pressure to give a yellow solid. The solid was recrystallized from CH<sub>3</sub>CN/Et<sub>2</sub>O (317 mg, 79% yield). <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN): δ (ppm) = 8.95 (d, *J* = 7.0 Hz, 4H), 8.31 (s, 2H), 8.18 (d, *J* = 7.0 Hz 4H), 7.33 (s, 2H), 7.30 (s, 2H), 3.77 (s, 6H). <sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>CN): δ (ppm) = 152.19, 139.76, 133.15, 129.15, 125.98, 125.52, 114.76, 36.87. ESI-MS [M]<sup>+</sup>: *m/z* 361 [Au(N-methylimidazole)<sub>2</sub>]<sup>+</sup>.

#### 4.11. Synthesis of **14**.

Au(1,3-dimethylbenzimidazole)Cl (300 mg, 0.79 mmol) was dissolved in 20 mL CH<sub>2</sub>Cl<sub>2</sub> followed by the addition of 640 μL of pyridine (7.9 mmol). AgOTf (203 mg, 0.79) was

added to the mixture and stirred overnight in the dark. The mixture was filtered through celite and the solvent was reduced to half *in vacuo*. Addition of Et<sub>2</sub>O (20 mL) to the mixture afforded a white solid which was washed with Et<sub>2</sub>O (3 X 5 mL). 81% yield. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN): δ (ppm) = 8.71 (d, *J* = 4.0 Hz, 2H), 8.18 (br, 1H), 7.78 (br, 2H), 7.69 (dd, *J* = 6.2, 3.1 Hz, 2H), 7.54 (dd, *J* = 6.2, 3.1 Hz, 2H), 4.12 (s, 6H). <sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>CN): δ (ppm) = 173.11, 152.54, 142.64, 134.86, 127.80, 125.74, 112.84, 36.10. ESI-MS [M]<sup>+</sup>: *m/z* 384.0 [Au(1,3-dimethylbenzimidazolole)(CH<sub>3</sub>CN)]<sup>+</sup>, 422.0 [Au(1,3-dimethylbenzimidazole)(pyridine)]<sup>+</sup>.

#### 4.12. Synthesis of 26.

A solution of **5H** (59 mg, 0.088 mmol) in CH<sub>3</sub>CN (2 mL) was added drop wise to a solution of **14** (50 mg, 0.088 mmol) in CH<sub>3</sub>CN (2 mL). The mixture was then stirred for 30 minutes giving a yellow solution. The solvent was removed under reduced pressure to give a yellow solid which was recrystallized from CH<sub>3</sub>CN/Et<sub>2</sub>O. (62 mg, 68% yield). <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN): δ (ppm) = 8.81 (d, *J* = 7.96 Hz, 4H), 8.44-8.40 (m, 4H), 8.33 (t, *J* = 7.72 Hz, 1H), 7.88 (t, *J* = 7.72, 4H), 7.78 (dd, *J* = 6.44, 3.16 Hz, 2H), 7.76-7.72 (m, 2H), 7.63 (dd, *J* = 6.32, 3.24 Hz, 2H), 4.18 (s, 6H). <sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>CN): δ (ppm) = 152.31, 150.87, 147.10, 145.79, 135.26, 131.59, 129.55, 128.16, 114.20, 36.11. ESI-MS [M]<sup>+</sup>: *m/z* 719.1 [Au(1,3-dimethylbenzimidazole)(pyridine)]<sup>3+</sup>[OTf]<sup>-2</sup>, 798.4 [Au(1,3-dimethylbenzimidazole)(pyridine)<sub>2</sub>]<sup>3+</sup>[OTf]<sup>-2</sup>, 877.8 [Au(1,3-dimethylbenzimidazole)(pyridine)<sub>3</sub>]<sup>3+</sup>[OTf]<sup>-2</sup>.

## Associated Content

**Supporting Information.** Experimental details with associated  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{31}\text{P}$  NMR spectra of synthesized compounds and reaction mixtures. Mass spectra of synthesized compounds and reaction mixtures. The X-ray structure refinements in .cif format have been deposited with the CCDC (1877082-1877089).

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Notes

The authors declare no competing financial interest.

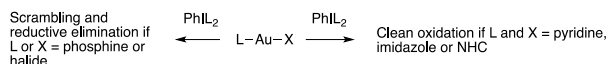
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## TOC Synopsis and Figure



Reactions of selected Au(I) coordination complexes with hypervalent I(III) reagents have been studied. The presence of monodentate phosphine ligands or halides is determined to be detrimental, with mixtures formed as a result of scrambling and reductive elimination processes, while reactions proceed cleanly if more difficult to oxidize pyridine, imidazole or NHC ligands are used.