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

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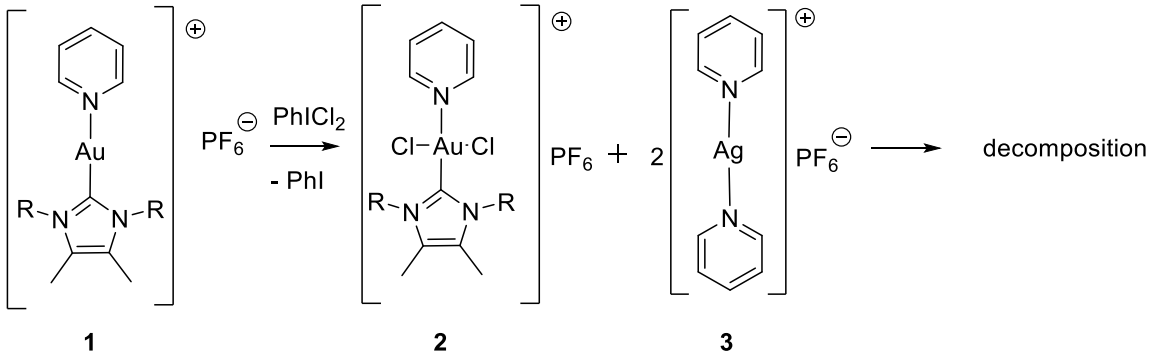
Abstract

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 $[Au(N\text{-}Me\text{-}imidazole)_2]^+$ and $[Au(pyridine)(NHC)]^+$ with iodine(III) reagents yielding a series of cationic gold(III) complexes. In contrast, reactions of phosphine ligated gold(I) complexes with iodine(III) reagents resulted in the oxidation of the phosphine ligand.

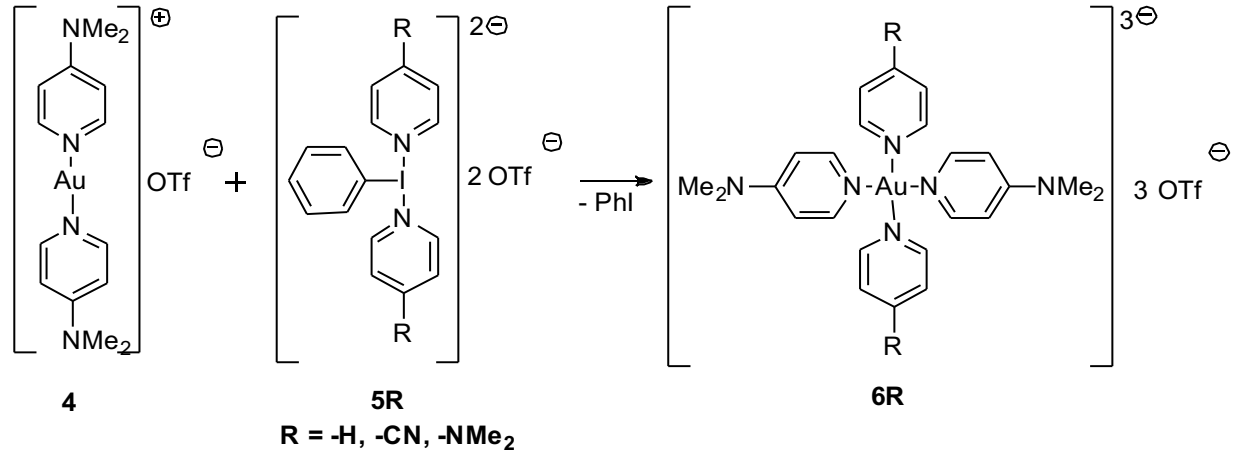
Introduction

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] 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.[3-9] In one report, Blank and de Frémont have displayed the use of $PhICl_2$ 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).[10]

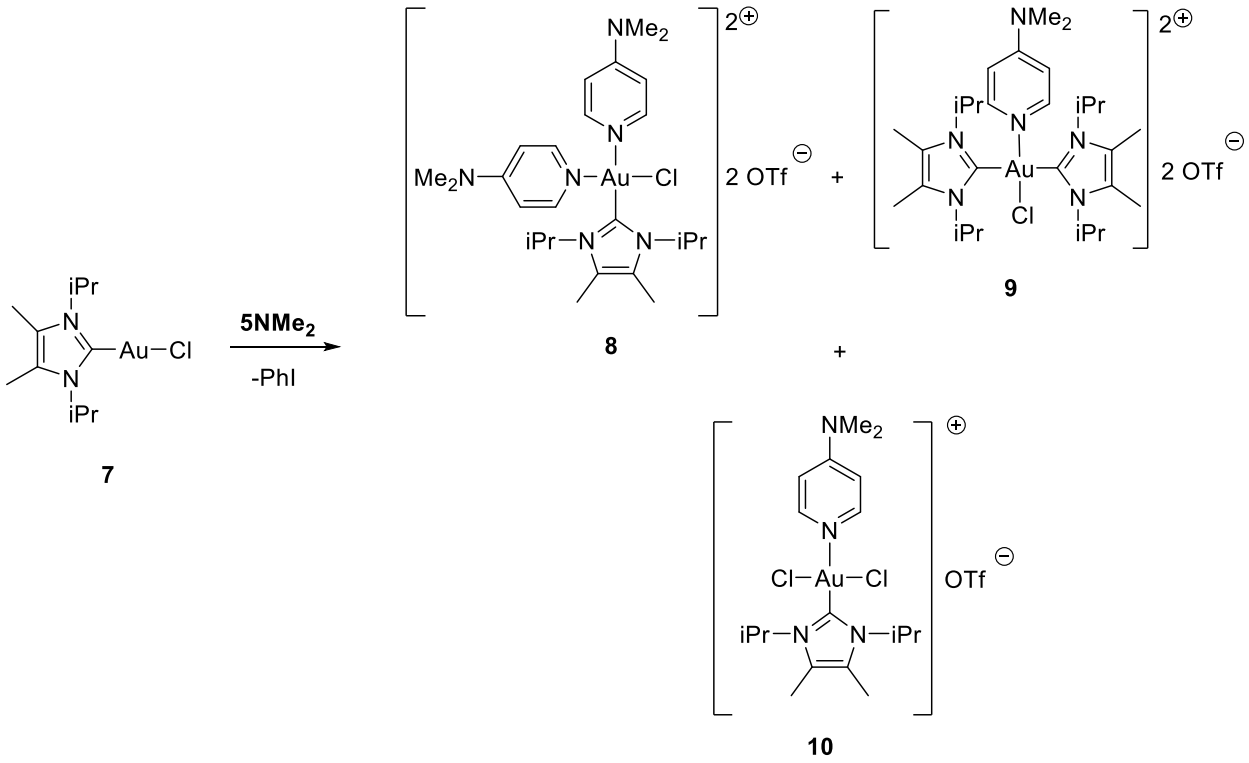


Scheme 1. Attempts to generate tricationic Au(III) complexes.

Our group has demonstrated the use of I(III) based reagents in accessing tricationic Au(III) complexes. These reagents have proved to be an effective oxidant for the synthesis of homoleptic and pseudo-homoleptic tricationic Au(III) complexes (Scheme 2). In the reaction of **4** with **5R,** compounds of the class **6R** were generated in high yields. In contrast, the reaction of NHC-Au(I)-Cl **7** with **5NMe$_2$** gave a complex mixture of products (**8**,**9** and **10**) arising from ligand exchange and anion scrambling (Scheme 3).[11]



Scheme 2. Synthesis of tricationic Au(III) complexes.



Scheme 3. Reaction of **7** with **5NMe$_2$**.

Previously our group reported that phosphine-containing Ir(I) (Vaska's complex) and Rh(I) (Wilkinson's catalyst) reacted with I(III) reagents also generally resulted in

scrambling. These starting materials bear a chloride ligand as did **7**. Reactions involving bidentate phosphines without halides went much more cleanly.

Direct reaction of 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.[12-14]

Based on these results, we hypothesized that scrambling is induced by the presence of a halide substituent, and have investigated the reactions of selected halide-free phosphine or NHC containing Au(I) complexes as well as N-bound Au(I) complexes 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) complexes without halides we are able to generate previously inaccessible mono-NHC-trispyridine trications.

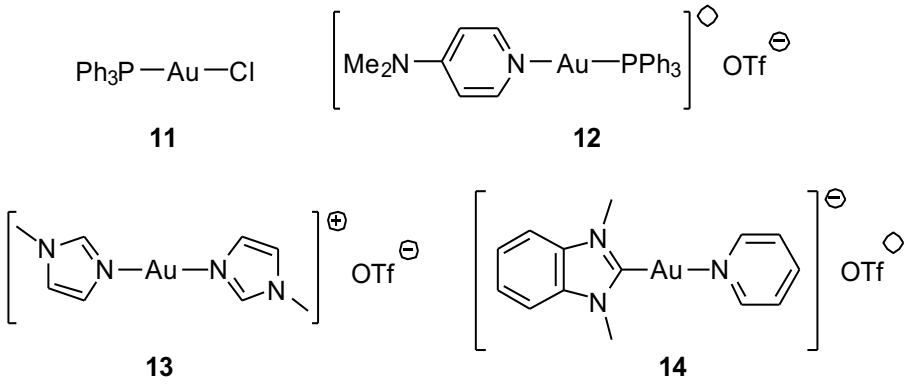
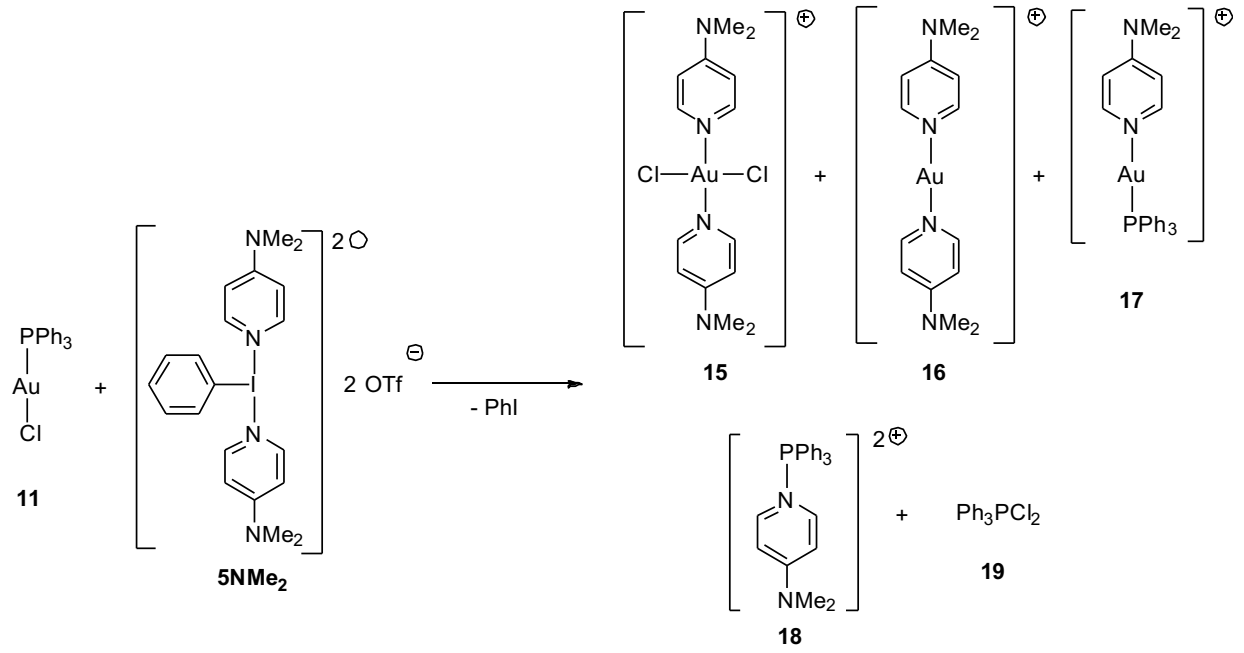


Figure 1. Au(I) complexes used in this study.

Results and discussion

Reactions of phosphine gold complexes.

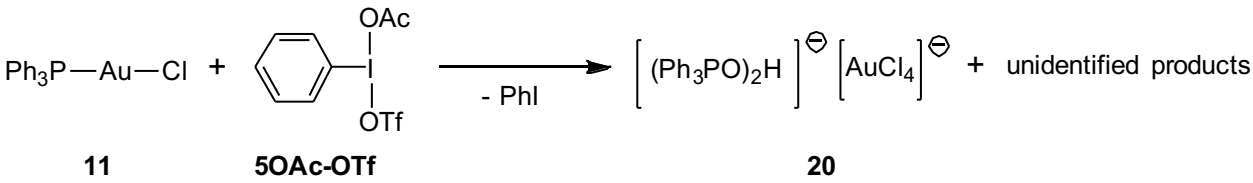
Reaction of **11** with **5NMe$_2$** in CD_3CN resulted in a color change to orange within 10 minutes. The ^{1}H NMR spectrum of the reaction mixture indicated that there was a complex mixture of products present. The ^{31}P NMR spectrum of the reaction mixture gave 4 peaks (65.6, 57.6, 33.0 and 29.9 ppm) indicating the presence of four phosphorus containing products. The peaks at 65.6 and 57.6 ppm are consistent with the reported compounds **18** and **19** respectively.[12, 15] The peaks at 33.0 and 29.9 are consistent with the gold compounds **11** and **17** respectively.[16-17] Positive mode ESI-MS detection of a CH_3CN solution of the reaction mixture gave fragments that could be identified at $[m/z]^+$ = 510.4 consistent with **15** and $[m/z]^+$ = 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$_2$** with the addition of products apparently arising from reductive elimination reactions.



Scheme 4. Reaction of **11** with **5NMe$_2$** outcome as identified by mass spectrometry and ^{31}P NMR.

The reaction of **11** with **5OAc-OTf** in a 1:1 ratio in $CHCl_3$ resulted in a color change to yellow instantly (Scheme 5). The ^{1}H NMR spectrum of the mixture indicated the presence of iodobenzene and one other species. The ^{31}P NMR of the solution had one singlet at 52.1 ppm. Searching the literature for potential oxidized phosphine products revealed that [Ph_3P-OTf][OTf] has been reported to give an identical chemical shift.[12] The Ph_3PO was not detected in the ^{31}P NMR of the crude reaction, but it can be rationalized by the reported behavior of [Ph_3P-OTf][OTf] where an equilibrium between [Ph_3P-OTf][OTf] and Ph_3PO + triflic anhydride was observed.[18-19] The positive ESI-MS detection of the mixture contained signal at $[m/z]^+$ = 556.1 corresponding to $[(Ph_3PO)_2H]^+$. X-Ray diffraction studies were done on single crystals obtained from vapor diffusion of Et_2O into concentrated CH_2Cl_2 solution revealed the crystal to be

compound **20** which consists of two Ph_3PO that are bridged with a proton and $[AuCl_4]^-$ (Figure 2).



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

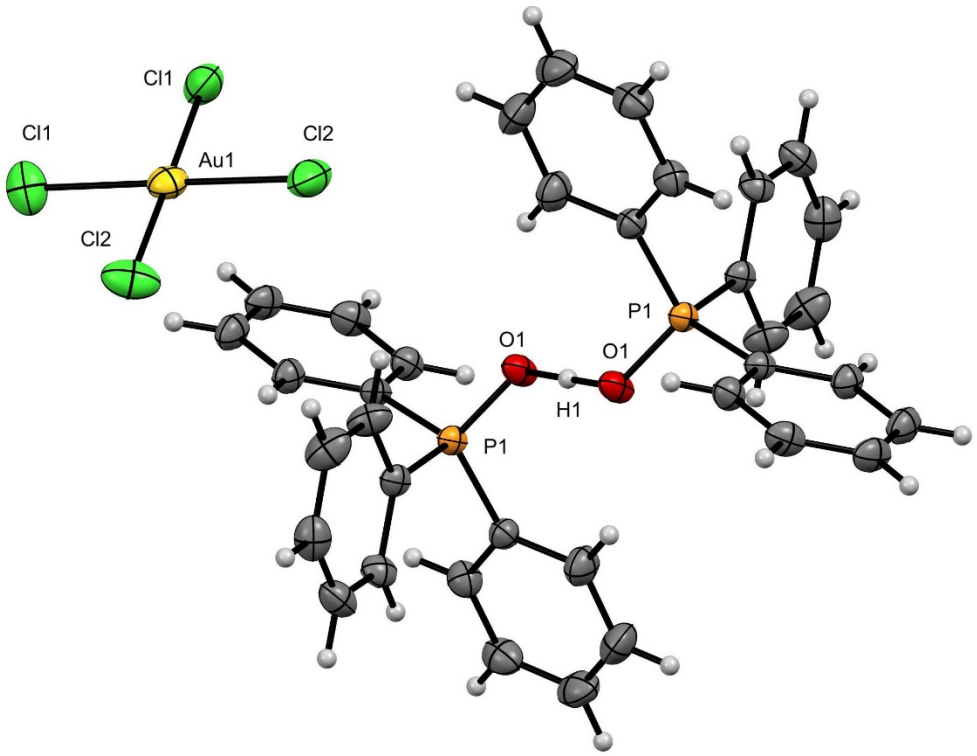
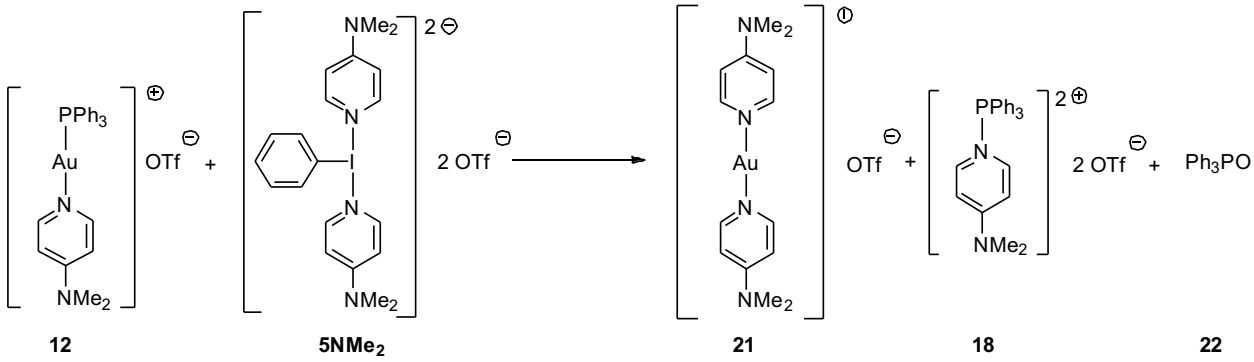


Figure 2. Solid-state structures of **20**. Thermal ellipsoids are drawn at the 50% probability level.

Treatment of compound **12** with **5NMe$_2$** resulted in a color change to orange within 10 minutes. The ^{31}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).[10, 12] The starting material (compound **12**) was also detected in the ^{31}P NMR at 29.7 ppm and in the cationic ESI mass spectrum of the reaction mixture ([m/z]$^+$ 580.0). The fragment in the ESI mass spectrum at [m/z]$^+$ = 440.8 is consistent with **21**.



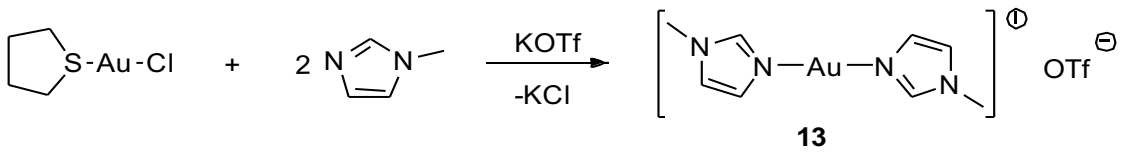
Scheme 6. Reaction of **12** with **5NMe$_2$** outcome as identified by mass spectrometry and ^{31}P NMR.

The reaction of **12** with **5OAc-OTf** resulted in color change to yellow instantly followed by the formation of a black solid. The ^{31}P NMR of the reaction mixture gave signals at 52.1 ppm representing [Ph_3P-OTf][OTf] and 27.8 ppm representing compound **22**. Positive mode ESI-MS detection of a CH_3CN solution of the reaction mixture gave fragments that could be identified at [m/z]$^+$ = 556.2 consistent with [$(PPh_3O)_2H$]$^+$ and [m/z]$^+$ = 499.4 consistent with [$Au(PPh_3)(CH_3CN)$]$^+$.

It's evident that the reactions of phosphine-containing gold(I) complexes with the selected I(III) resulted in the oxidation of PPh_3 and no phosphine-Au(III) complexes were isolated. Reaction of **12** with $PhICl_2$ (**5Cl**) was not attempted as this reaction (using pyridine-Au(I) instead of 4-DMAP-Au(I) as starting material) was previously reported and gave similar scrambling patterns to what has been observed in our reactions.[10]

Reactions of N-imidazole Au(I) complexes

The Au(I) starting complex **13** was achieved *via* adapting the synthetic protocol of Lin[20] and using N-methylimidazole as the ligand in place of 4-DMAP (Scheme 7). The same cation has previously been reported as an $[AuCl_2]^-$ salt.[21] 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 3).



13

Scheme 7. Synthesis of compound **13**

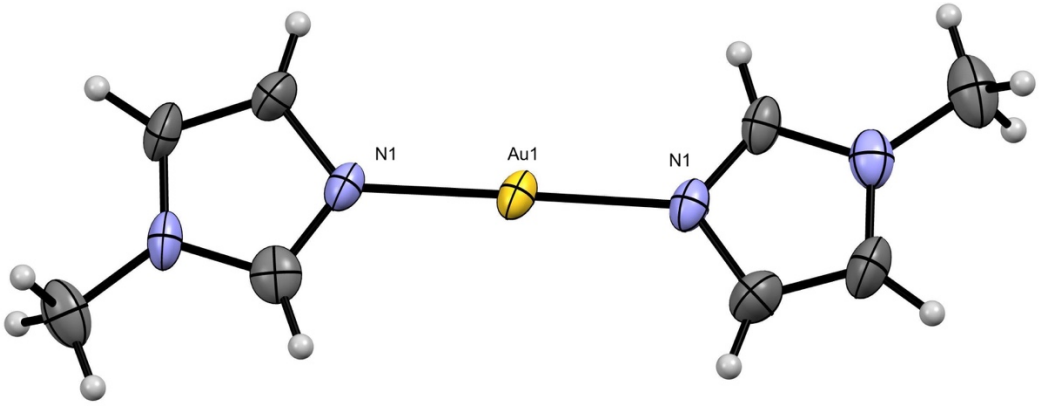
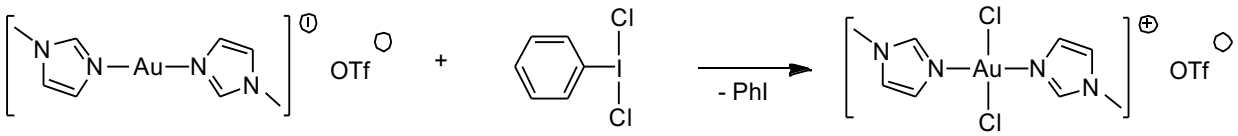


Figure 3. Solid-state structures of **13**. Thermal ellipsoids are drawn at the 50% probability level. Anions and solvate were omitted for clarity (OTf, CH_3CN). Selected bond distances (Å) Au1-N1 2.000(7).

Reaction of **13** with **5Cl** in CH_2Cl_2 resulted in the formation of a yellow solid. The solid was filtered and washed with CH_2Cl_2. ^1H NMR analysis of the solid in CD_3CN gave a set of resonances consistent with a single N-methylimidazole containing product (Scheme 8). Mass spectrometry in CH_3CN showed signals arising from compound **23** which was further confirmed by X-Ray diffraction studies on single crystals obtained from vapor diffusion of Et_2O into concentrated CH_3CN solution of the isolated solid **(**Figure 4).



13 **5Cl** **23**

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

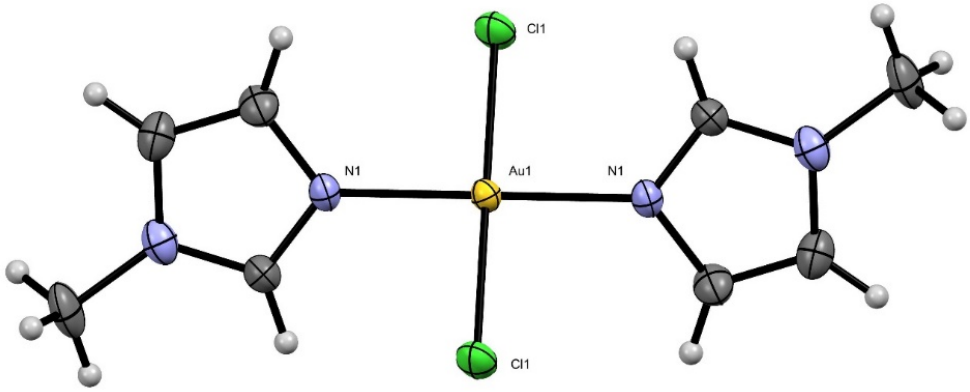
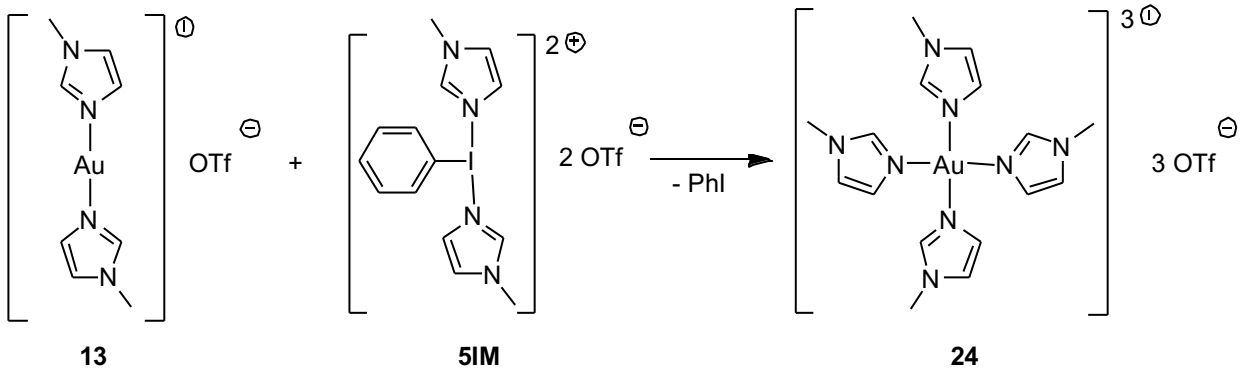


Figure 4. Solid-state structures of **23**. Thermal ellipsoids are drawn at the 50% probability level. Anions and solvate were omitted for clarity (OTf, CH_3CN). Selected bond distances (Å) Au1-N1 2.007(6), Au1-Cl1 2.277(17).

Reaction of **13** with **5IM** in CH_3CN (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_3CN/Et_2O.



13 **5IM** **24**

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

^1H 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 $[Au(N\text{-methylimidazole})_4\ 2OTf]^+$. Single crystals were grown from a CH_3CN solution of the compound via slow vapor diffusion of Et_2O and subsequent X-ray diffraction studies confirmed homoleptic compound **24** (Figure 5), which is isolated in 79% yield. This compound is the second example of homoleptic N-imidazole containing Au(III) trications. The first reported example incorporated an extended Au-ligand framework for the synthesis of Au nanoparticles.[22]

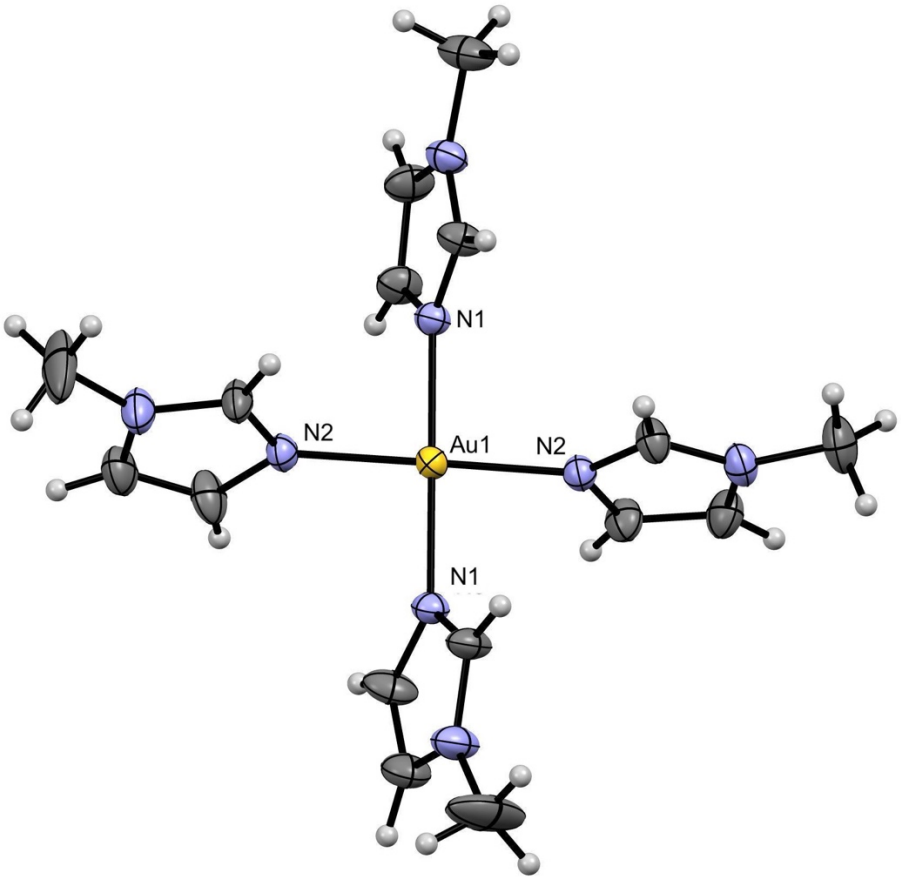
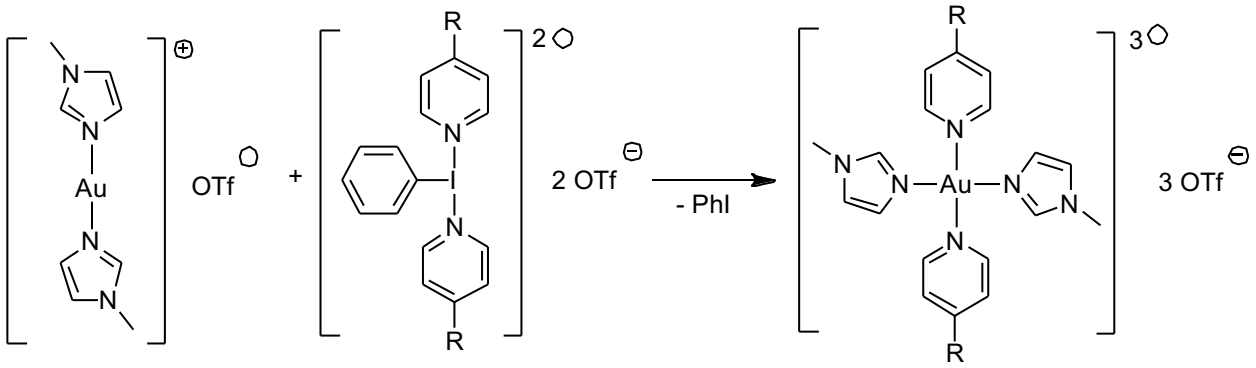


Figure 5. Solid-state structures of **24**. Thermal ellipsoids are drawn at the 50% probability level. Anions and solvate were omitted for clarity (OTf, CH_3CN). Selected bond distances (Å) Au1-N1 1.996(3), Au1-N2 1.999(3).

Using I(III) oxidant **5R** resulted in the corresponding pseudo-homoleptic compounds **25H, 25CN** and **25NMe$_2$** 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.[23] The solid state structures of compounds **25H** and **25CN** are depicted in Figures 6 and 7. Unfortunately no crystals of diffraction quality could be obtained for compound **25NMe$_2$**.

The reaction of **5OAc-OTf** with **13** in $CHCl_3$ resulted in a decomposition of the Au complex which was indicated by the formation of black solid.



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

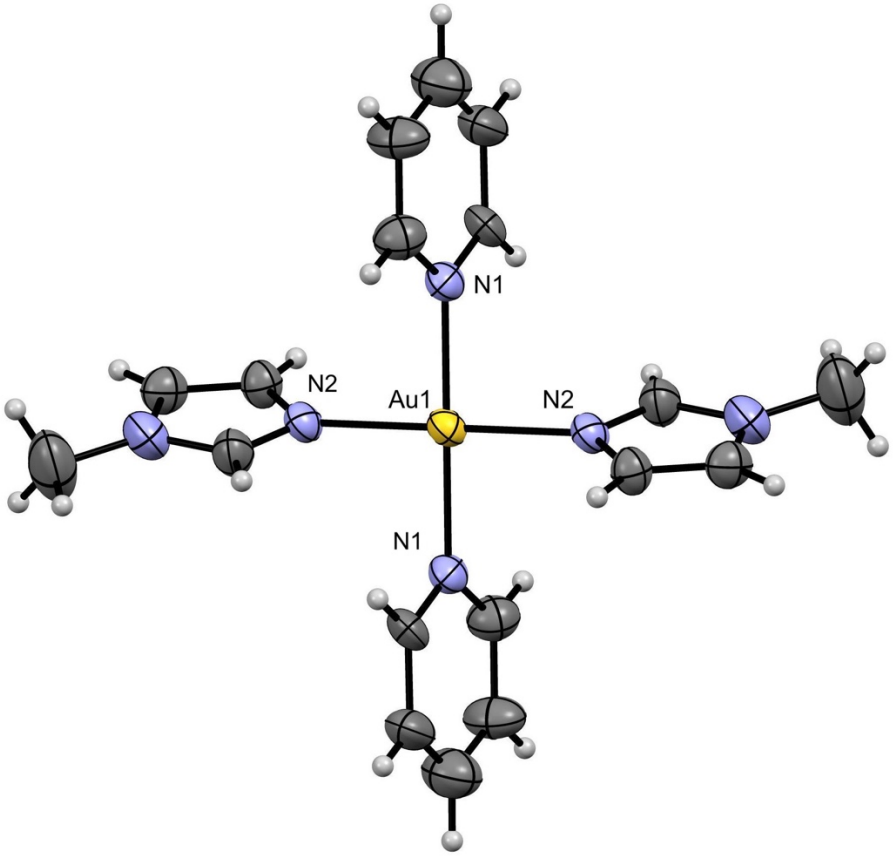


Figure 6. Solid-state structures of **25H**. Thermal ellipsoids are drawn at the 50% probability level. Anions and solvate were omitted for clarity (OTf, CH_3CN). Selected bond distances (Å) Au1-N1 2.016(5), Au1-N2 2.009(4).

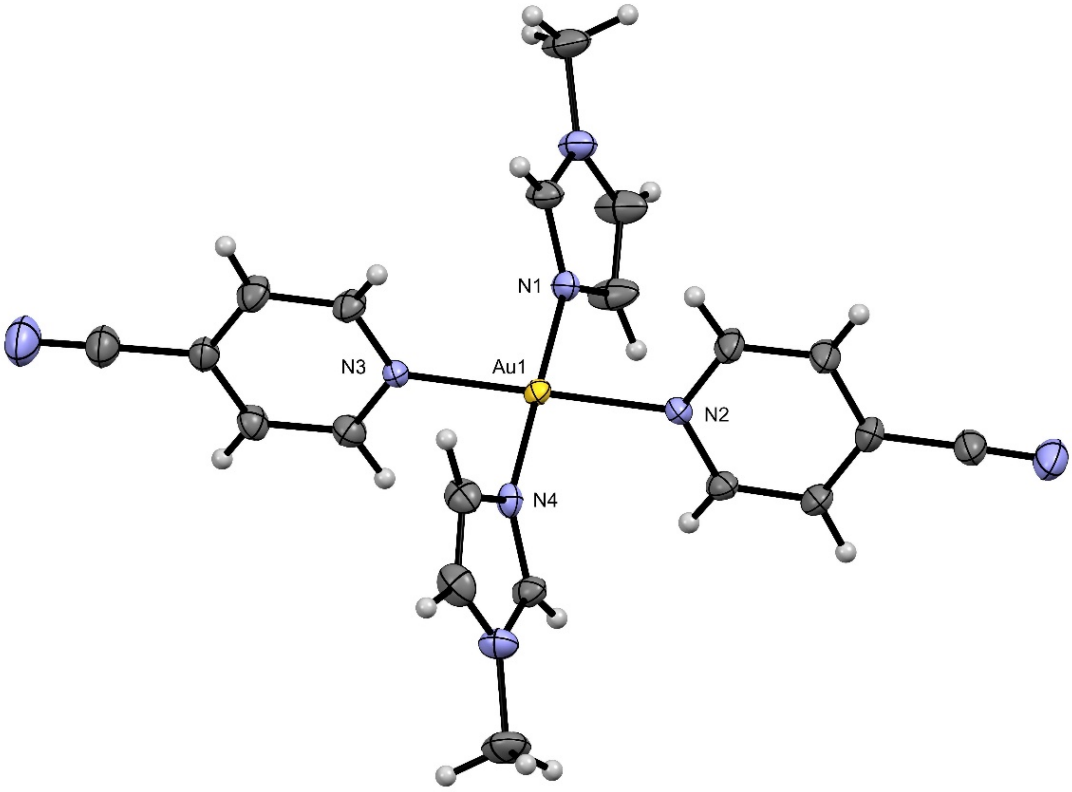
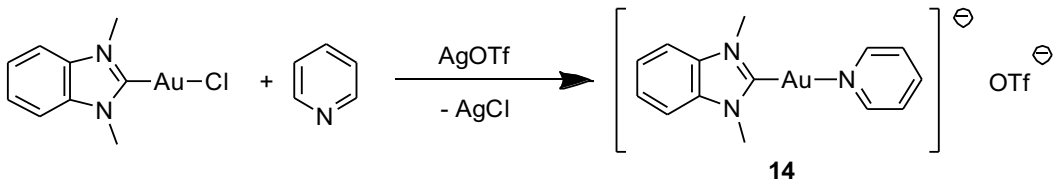


Figure 7. Solid-state structures of **25CN**. Thermal ellipsoids are drawn at the 50% probability level. Anions and solvate were omitted for clarity (OTf, CH_3CN). Selected bond distances (Å) Au1-N1 2.006(4), Au1-N2 2.035(4), Au1-N3 2.024(4), Au1-N4 1.991(4).

The starting complex **14** was synthesized using the standard synthetic protocol of de Frémont [10] and using 1,3-dimethylbenzimidazolium as the ligand (Scheme 11). The solid state structure of **14** is shown in Figure 8.



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

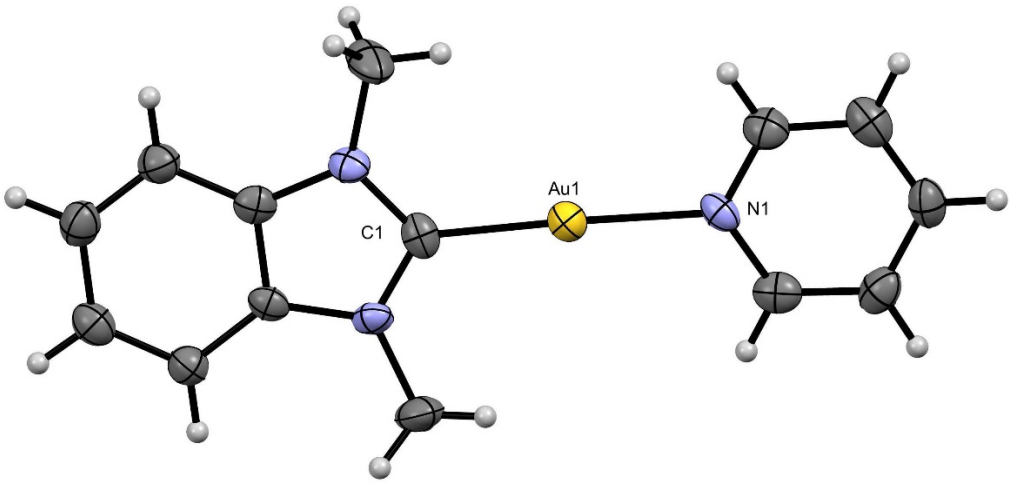
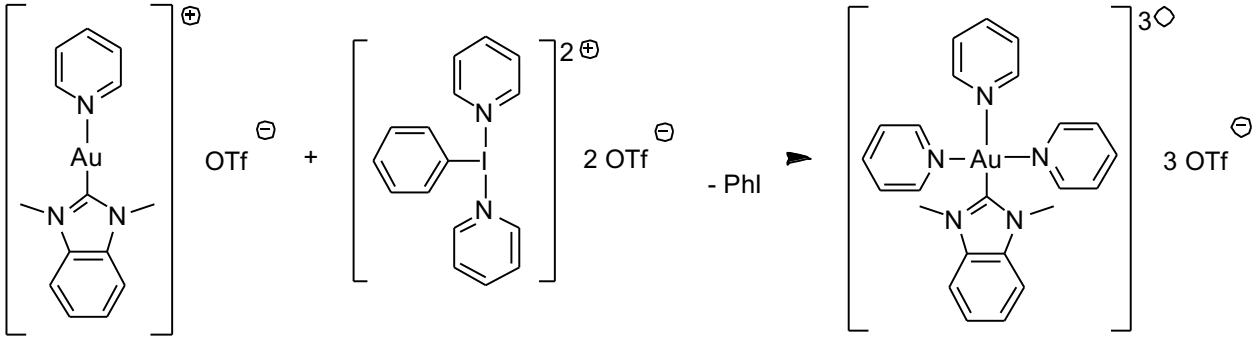


Figure 8. Solid-state structures of **14**. Thermal ellipsoids are drawn at the 50% probability level. Anions and solvate were omitted for clarity (OTf, CH_3CN). Selected bond distances (Å) Au1-N1 2.052(5), Au1-C1 1.975(7).

Reaction of **14** with $PhICl_2$ was not attempted as similar reactions were previously reported on Au(I) compounds with different NHC ligands.[10] Treatment of compound **14** with **5H** in CD_3CN at room temperature for 30 minutes followed by workup resulted in the isolation of a yellow solid. The ^1H NMR spectroscopy of the isolated solid was consistent with a single compound containing one 1,3-dimethylbenzimidazole and three

pyridine ligands (Scheme 12). The positive ESI-MS detection of the mixture indicated the presence of **26** at $[m/z]^+$= 877.8 as monocationic $[Au(NHC)(pyridine)_3\ 2OTf]^+$.



14 **5H** **26**

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

X-Ray diffraction studies were done on single crystals obtained from vapor diffusion of Et_2O into concentrated CH_3CN solution of the isolated solid confirmed the compound to be **26**.

Reaction of **14** with **5OAc-OTf** in $CDCl_3$ resulted in the formation of black solid due to decomposition of Au complex.

The synthesis of Au(III) cationic complexes (**23-26)** was achieved in good yield 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.[10]

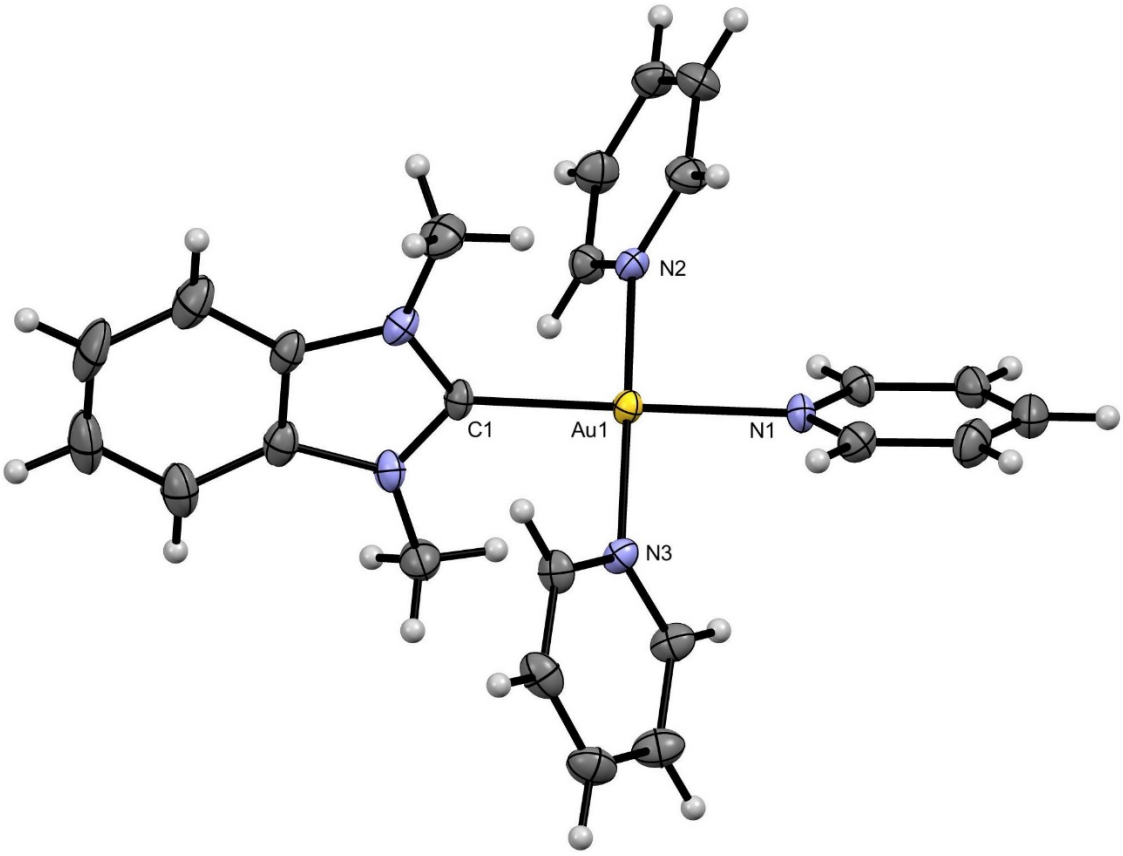


Figure 9. Solid-state structures of **26**. Thermal ellipsoids are drawn at the 50% probability level. Anions and solvate were omitted for clarity (OTf, CH_3CN). Selected bond distances (Å) Au1-N1 2.085(3), Au1-N2 2.025(3), Au1-N3 2.021(3), Au1-C1 2.032(3).

Conclusion

This work described the synthesis of a series of cationic Au(III) complexes. Oxidative addition to N-bound Au(I) complex (**13**) using I(III) reagents resulted in homoleptic and pseudo-homoleptic Au(III) complexes in high yields. The reaction of **5H** with **14** generated mono-NHC-trispyridine Au(III) trications. In contrast, reactions of I(III) reagents with Phosphine-containing Au(I) complexes resulted in the oxidation of

phosphine and/or ligand scrambling.

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 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 CaH_2 and stirred for 2 days and distilled and then stored in the glove box over 3Å molecular sieves. Compounds **11**,[24] **12**,[17] **13**,[20] **14**,[10] **5Cl**[25] and **5R**[26] were synthesised via literature procedures. Gold powder was purchased from Precious Metals Online. All other reagents were purchased from Alfa Aesar or Sigma Aldrich and used as received.

Reaction of 11 with 5NMe$_2$. A solution of **5NMe$_2$** (82 mg, 0.11 mmol) in 3 mL CD_3CN was added drop wise to **11** (50 mg, 0.10 mmol) in 3 mL CD_3CN. The mixture was stirred for 3 hours resulting in a color change to orange. Aliquot was removed for NMR and mass spectrometry analysis. ^{31}P NMR (162 MHz, $CDCl_3$) δ (ppm): 65.6 (s), 57.6 (s), 33.0 (s), 29.9 (s). ESI-MS $[M]^{n+}$: m/z 273.8 $[Au(CH_3CN)Cl]^+$, 440.8 $[Au(4\text{-}dmap)_2]^+$, 510.4 $[Au(4\text{-}dmap)_2Cl_2]^+$. See supporting information for ^1H NMR.

Reaction of 11 with 5OAc-OTf. A mixture of diacetoxyiodobenzene (20.6 mg, 0.064 mmol) and TMS-OTf (23.3 µL, 0.128 mmol) in 2 mL $CHCl_3$ was added drop wise to a solution of **11** (30 mg, 0.061 mmol) in 2 mL $CHCl_3$. 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 Et_2O. ^{31}P NMR (162 MHz, CD_3CN) δ (ppm): 52.1 (s). ESI-MS $[M]^{n+}$: m/z 273.8 $[Au(CH_3CN)Cl]^+$, 556.1 $[(Ph_3PO)_2H]^+$. ^1H NMR (400 MHz, CD_3CN): δ (ppm) = 7.91-7.87 (m), 7.78-7.70 (m).

Reaction of 12 with 5NMe$_2$. A solution of **5NMe$_2$** (52 mg, 0.070 mmol) in 2 mL CH_3CN was added to a solution of **12** (50 mg, 0.068 mmol) in 2 mL CH_3CN 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 Et_2O. ^{31}P NMR (162 MHz, CD_3CN) δ (ppm): 57.6 (s), 29.7 (s), 26.6 (s). ESI-MS $[M]^{n+}$: m/z 395.0 $[Ph_3P]^{2+}[Tf]^-$, 440.8 $[Au(4\text{-dmap})_2]^+$, 499.4 $[Au(PPh_3)(CH_3CN)]^+$, 580.0 $[Au(PPh_3)(4\text{-dmap})]^+$, 736.2 $[Au(PPh_3)(Ph_3PO)]^+$. See supporting information for ^1H NMR.

Reaction of 12 with 5OAc-OTf. A mixture of diacetoxyiodobenzene (20.6 mg, 0.064 mmol) and TMS-OTf (23.3 µL, 0.128 mmol) in 2 mL $CHCl_3$ was added drop wise to **12** (45 mg, 0.062 mmol) in 2 mL $CHCl_3$ 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}P NMR (162 MHz, $CHCl_3$) δ (ppm): 52.1 (s), 27.8 (s). ESI-MS $[M]^+$: *m/z* 556.2 $[(PPh_3O)_2H]^+$, 499.4 $[Au(PPh_3)(CH_3CN)]^+$.

Synthesis of 13. N-methylimidazole (175 µL, 2.20 mmol) was added to a dichloromethane solution (20 mL) containing 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 Et_2O and

recrystallized from CH_2Cl_2/ Et_2O to give a white solid (457 mg, 82%). ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.26 (s, 2H), 7.13 (s, 2H), 7.05 (s, 2H), 3.84 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 141.00, 129.44, 121.71, 35.23. ESI-MS $[M]^+$: *m/z* 361 $[Au(N\text{-methylimidazole})_2]^+$.

Synthesis of 23. A solution of **5Cl** (27 mg, 0.098 mmol) in 2 mL CH_2Cl_2 was added drop wise to a solution of **13** (50 mg, 0.098 mmol) in 2 mL CH_2Cl_2. The mixture was then stirred for 30 minutes resulting in a yellow solid. The solid was filtered, washed with CH_2Cl_2 (3 X 3 mL) and dried *in vacuo* (49 mg, 85 yield). ^1H NMR (400 MHz, CD_3CN): δ (ppm) = 8.30 (s, 2H), 7.39 (s, 2H), 7.35 (s, 2H), 3.86 (s, 6H). ^{13}C NMR (100 MHz, CD_3CN): δ (ppm) = 139.69, 127.74, 123.89, 36.54. ESI-MS $[M]^+$: *m/z* 361.0 $[Au(N\text{-methylimidazole})_2]^+$, 395.0 $[Au(N\text{-methylimidazole})_2Cl]^+$ 431.0 $[Au(N\text{-methylimidazole})_2Cl_2]^+$.

Synthesis of 24. A solution of **5IM** (66 mg, 0.098 mmol) in 2 mL CD_3CN was added drop wise to a solution of **13** (50 mg, 0.098 mmol) in 2 mL CD_3CN. 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_2O to afford a yellow solid. The solid was then washed with Et_2O (3 X 3 mL) and dried *in vacuo* (76 mg, 70% yield). ^1H NMR (400 MHz, CD_3CN): δ (ppm) = 8.20 (s, 4H), 7.32 (s, 4H), 7.20 (s, 4H), 3.80 (s, 12H). ^{13}C NMR (100 MHz, CD_3CN): δ (ppm) = 139.50, 126.53, 124.76, 36.66. ESI-MS $[M]^+$: *m/z* 361.1 $[Au(N\text{-methylimidazole})_2]^+$, 823.1 $[Au(N\text{-methylimidazole})_4]^{3+}$ $[OTf]_2^-$.

Synthesis of 25NMe$_2$. A solution of **5NMe$_2$** (74 mg, 0.098 mmol) in 2 mL CD_3CN was added drop wise to a solution of **13** (50 mg, 0.098 mmol) in 2 mL CD_3CN 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_2O to afford a yellow solid. The solid was then washed with Et_2O (3 X 3 mL) and dried *in vacuo* (78 mg, 76% yield). ^{1}H NMR (400 MHz, CD_3CN): 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). ^{13}C NMR (100 MHz, CD_3CN): δ (ppm) = 157.02, 147.10, 139.46, 126.26, 124.98, 110.25, 40.24, 36.70. ESI-MS $[M]^+$: *m/z* 361.1 $[Au(N\text{-methylimidazole})_2]^+$, 401.1 $[Au(N\text{-methylimidazole})(4\text{-dmap})]^+$, 441.1 $[Au(4\text{-dmap})_2]^+$, 902.9 $[Au(N\text{-methylimidazole})_2(4\text{-dmap})_2]^+[OTf]_2^-$.

Synthesis of 25H. A solution of **5H** (65 mg, 0.098 mmol) in 2 mL CD_3CN was added drop wise to a solution of **13** (50 mg, 0.098 mmol) in 2 mL CD_3CN 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_2O to afford a yellow solid. The solid was then washed with Et_2O (3 X 3 mL) and dried *in vacuo* (68 mg, 72% yield). ^{1}H NMR (400 MHz, CD_3CN): 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). ^{13}C NMR (100 MHz, CD_3CN): δ (ppm) = 150.75, 146.29, 139.56, 130.62, 125.92, 125.40, 36.76. ESI-MS $[M]^+$: *m/z* 358.1 $[Au(N\text{-methylimidazole})(pyridine)]^+$, 361.1 $[Au(N\text{-methylimidazole})_2]^+$, 816.5 $[Au(N\text{-methylimidazole})_2(pyridine)_2]^{3+}[OTf]^-_2$.

Synthesis of 25CN A solution of **5CN** (278 mg, 0.392 mmol) in CH_3CN (5 mL) was added drop wise to a solution of of **13** (200 mg, 0.392 mmol) in CH_3CN (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_3CN/Et_2O **(**317 mg, 79% yield). ^1H NMR (400 MHz, CD_3CN): 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). ^{13}C NMR (100 MHz, CD3CN): δ (ppm) = 152.19, 139.76, 133.15, 129.15, 125.98, 125.52, 114.76, 36.87. ESI-MS $[M]^+$: m/z 361 $[Au(N\text{-methylimidazole})_2]^+$.

Synthesis of 14. Au(1,3-dimethylbenzimidazole)Cl (300 mg, 0.79 mmol) was dissolved in 20 mL CH_2Cl_2 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_2O (20 mL) to the mixture afforded a white solid which was washed with Et_2O (3 X 5 mL). 81% yield. ^1H NMR (400 MHz, CD_3CN): 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). ^{13}C NMR (100 MHz, CD3CN): δ (ppm) = 173.11, 152.54, 142.64, 134.86, 127.80, 125.74, 112.84, 36.10. ESI-MS $[M]^+$: m/z 384.0 $[Au(1,3\text{-dimethylbenzimidazolole})(CH_3CN)]^+$, 422.0 $[Au(1,3\text{-dimethylbenzimidazole})(pyridine)]^+$.

Synthesis of 26. A solution of **5H** (59 mg, 0.088 mmol) in CH_3CN (2 mL) was added drop wise to a solution of **14** (50 mg, 0.088 mmol) in CH_3CN (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_3CN/Et_2O. (62 mg, 68% yield). ^1H NMR (400 MHz, CD_3CN): 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). ^{13}C NMR (100 MHz, CD3CN): δ (ppm) = 152.31, 150.87, 147.10, 145.79, 135.26, 131.59, 129.55, 128.16, 114.20, 36.11. ESI-MS $[M]^+$: m/z 719.1 [Au(1,3-dimethylbenzimidazole)(pyridine)]$^{3+}$[OTf]$^-_2$, 798.4 [Au(1,3-dimethylbenzimidazole)(pyridine)$_2$]$^{3+}$[OTf]$^-_2$, 877.8 [Au(1,3-dimethylbenzimidazole)(pyridine)$_3$]$^{3+}$[OTf]$^-_2$.

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