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Research Article

DOI: <http://dx.doi.org/10.22192/ijcrpps.2016.03.12.003>**A novel series of Gold(III)-mesitylene-arylazimidazole  
and diphosphine complexes: Synthesis and  
Spectroscopic analysis.****Prithwiraj Byabartta**Inorganic Chemistry Research Laboratory, Department of Chemistry, Jogesh Chandra Chaudhuri College,  
30- Prince Anwar Shah Road, Kolkata-700033;\*Corresponding Author: [pribatta@rediffmail.com](mailto:pribatta@rediffmail.com)**Abstract**

The reaction between  $\text{PPN}[\text{AuCl}_4]$  and  $[\text{Hg}(\text{mes})_2]$  gives the anionic complex  $\text{cis-PPN}[\text{Au}(\text{mes})_2\text{Cl}_2]$  (**1**) and  $[\text{Hg}(\text{mes})\text{Cl}]$  as side-product. Complex **1** is a precursor to other compounds both neutral and cationic. The twelve new complexes,  $\text{cis-}[\text{Au}(\text{mes})_2(\text{L-L})]\text{X}$  ( $\text{L-L}=\text{RaaiR}'$  (**1a-1i**),  $\text{L-L}=\text{dppe}$  (**3**),  $\text{L-L}=\text{dppm}$  (**2**),  $\text{L-L}=\text{dppa}$  (**4**),  $\text{X}=\text{SO}_3\text{CF}_3$ ) are characterised by ES/MS, IR and multinuclear NMR ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{19}\text{F}$ ,  $^{31}\text{P}$ ) spectroscopic studies. In addition by dimensional NMR studies as  $^1\text{H}$   $^1\text{H}$  COSY and  $^1\text{H}$   $^{13}\text{C}$  HMQC permit a complete assignment of the complexes in the solution phase.

**Keywords:** Gold(III), 1-alkyl-2-(arylo)imidazole,  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{19}\text{F}$ ,  $^{31}\text{P}$  COSY, HMQC NMR.

**1. Introduction**

Gold(III) complexes with two gold-carbon bonds have been known for a long time, particularly those containing methyl or pentafluorophenyl groups as ligands [1, 2, 3, 4]. The traditional synthesis with Grignard or organolithium reagents lead generally to very low yields. Improved synthetic methods involved the use of organotin, organothallium [6] and organomercury [7,8] reagents or, in a few cases, the oxidative addition of halogen to the corresponding organogold(I) complexes  $[\text{AuR}_2]$  [9,10]. We have been reporting on the chemistry of mesityl gold(I) derivatives [11,12,13]. The radical mesityl  $[(\text{C}_6\text{H}_2\text{Me}_3)-]$  can act as a simple (terminal) ligand or as a bridge between two metallic centres affording a three-centre two-electron bond. Mesityl gold(I) derivatives of the type  $[\text{AuRL}]$  have proven to be useful precursors to homo- and hetero-polynuclear compounds that have displayed interesting metal-metal interactions. We wanted to extend this chemistry to gold(III) complexes and study the behaviour of such compounds. Gold(III) compounds containing the mesityl

group as a terminal ligand have been obtained by reaction between the Grignard reagent and  $[\text{AuCl}_2(\text{L-L})]\text{ClO}_4$  [ $\text{L-L}=\text{bipy}$  (2,2-bipyridine), phen (1,10-phenanthroline)] and by oxidative addition of halogens to mesityl gold(I)  $\text{Q}[\text{Au}(\text{mes})\text{X}]$  complexes ( $\text{Q}=\text{P}(\text{CH}_2\text{Ph})\text{PPh}_3$ ,  $\text{N}(\text{PPh}_3)_2$ ) [11]. However, both methods have restrictions. It was, therefore, desirable to obtain a mesityl gold(III) compound that could be used as a precursor to other gold(III) products in a wider range. In this paper we describe the synthesis of the compound  $\text{cis-PPN}[\text{Au}(\text{mes})_2\text{Cl}_2]$  (**1**) ( $\text{PPN}^+:\text{N}(\text{PPh}_3)_2$ , bis(triphenylphosphine)iminium) which is obtained via the organomercury reagent  $[\text{Hg}(\text{mes})_2]$  [1-7, 27-57] according to an earlier procedure for transferring one or two aryl groups to gold(III) centres [7,8,16,17,18,19,23,24-26, 58-96]. Complex **1** behaves as a precursor to other mesityl gold(III) compounds both neutral and cationic. In this article we have synthesised a novel series of Gold(III) mesitylene square planar complexes with arylazimidazole linkage and the

complexes were well characterised by CHN analysis, IR, multinuclear NMR and ESI mass spectrophotometrically.

## 2. Experimental

### 2.1. Materials and Physical measurements

Instrumentation and general experimental techniques were as described earlier [11]. Proton and  $^{31}\text{P}\{^1\text{H}\}$ -NMR were described in detail in the Experimental Section. All the reactions were performed at room temperature (r.t.) except that of  $\text{PPN}[\text{AuCl}_4]$  with  $\text{Hg}(\text{mes})_2$ . Reactions of **1** with silver salts must be carried out avoiding light exposure until the silver chloride is removed. The starting materials  $\text{PPN}[\text{AuCl}_2]$  and  $[\text{Hg}(\text{mes})_2]$  were prepared as described previously.  $\text{PPN}[\text{AuCl}_4]$  was prepared by addition of stoichiometric  $\text{Cl}_2$  to a solution of  $\text{PPN}[\text{AuCl}_2]$  in dichloromethane. All other chemicals, ligand(RaaiR) [20-23] and organic solvents used for preparative work were of reagent grade (SRL, Sigma Alhrich). Microanalytical data (C, H, N) were collected using a Perkin Elmer 2400 CHN instrument. I.R. spectra were obtained using a Perkin Elmer spectrophotometer (using KBr disks,  $4000\text{--}350\text{ cm}^{-1}$ ). The  $^1\text{H}$  nmr spectra in  $\text{CDCl}_3$  were obtained on a Bruker 500 MHz FT NMR spectrometer using  $\text{SiMe}_4$  as internal reference,  $\text{CFCl}_3$  (external  $^{19}\text{F}$ ). Mass spectra were recorded on VG Autospec FAB technique using 3-nitrobenzyl(NBA) as matrix.

**Caution:** perchlorate salts of metal complexes with organic ligands are potentially explosive. So here all are of troflate salts.

#### 2.2.1. cis-PPN[Au(mes)<sub>2</sub>Cl<sub>2</sub>] (1)

To  $\text{PPN}[\text{AuCl}_4]$  (1.097 g, 1.25 mmol) in acetone (50 ml) was added  $[\text{Hg}(\text{mes})_2]$  (1.369 g, 3.12 mmol). After heating at reflux for 1.5 h, the yellow mixture became a yellow solution by solubilisation of the organomercury reagent. Heating for a further 4.5 h afforded a colourless solution. The reaction was usually stopped after 10 h of refluxing (when decomposition to metallic gold started to be noticed). The solution was cooled and filtered through Celite. The almost colourless solution was concentrated in vacuo to ca. 5 ml, and  $\text{Et}_2\text{O}$  (20 ml) added to precipitate **1** as a white solid. The analytical sample was purified by recrystallization from dichloromethane–ether. The  $\text{Et}_2\text{O}$  filtrate was concentrated in vacuo to ca. 5 ml, and *n*-hexane (20 ml) added to afford  $[\text{Hg}(\text{mes})\text{Cl}]$  as a white solid.

#### 2.2.2. cis-[Au(mes)<sub>2</sub>(L-L)]X (L-L=RaaiR<sup>+</sup> (1a-1i), L-L=dppe (3) L-L=dppm (2) L-L=dppa (4), X=SO<sub>3</sub>CF<sub>3</sub>)

To separate solutions of cis-PPN[Au(mes)<sub>2</sub>Cl<sub>2</sub>], **1** (0.1047 g, 0.1 mmol) in dichloromethane (20 ml) solutions of AgOTf (0.0514 g, 0.2 mmol) to obtain cis-PPN[Au(mes)<sub>2</sub>(OTf)<sub>2</sub>]. After removal of AgCl and PPN[X]

(X= TfO) in diethyl ether (20 ml) respectively added the ligand, HeaaiMe (0.0186 g, 0.1 mmol, **1a**), MeaaiMe (0.020 g, 0.1 mmol, **1b**), Claaime (0.0220 g, 0.1 mmol, **1c**), HaaiEt (0.020 g, 0.1 mmol, **1d**), MeaaiEt (0.0214 g, 0.1 mmol, **1e**), ClaaieEt (0.0235 g, 0.1 mmol, **1f**), HaaiBz (0.0262 g, 0.1 mmol, **1g**), MeaaiBz (0.0276 g, 0.1 mmol, **1h**), ClaaieBz (0.0297 g, 0.1 mmol, **1i**), dppe (0.0398 g, 0.1 mmol, **3**), dppm (0.0384 g, 0.1 mmol, **2**), dppa (0.0385 g, 0.1 mmol, **4**) were added. All these compounds (**1a-1i**, **2**, **3**, **4**) precipitated in the media and were separated by filtration as white solids for **2**, **3**, **4** and orange for **1a-1i** complexes.

Analysis for cis-[Au(mes)<sub>2</sub>(HaaiMe)](OTf), **1a**,  $[\text{C}_{29}\text{H}_{32}\text{N}_4\text{Au}](\text{SO}_3\text{F}_3)$ , Calc(found): C, 45.14 (45.8), H, 4.2 (4.4), N, 7.36(7.30); IR  $\nu(\text{N}=\text{N})$  1370  $\nu(\text{C}=\text{N})$  1590  $\nu(\text{mes})$  1586(w), 849(m,Br),  $\nu(\text{OTf})$  1260(br),1225(s), 1156(s), ES/MS, 770  $[\text{M}^+]$ , 620  $[\text{M-OTf}]$ ; Proton n.m.r.,  $^1\text{H}$ , ppm, 2.11(o-Mes), 2.21(p-Mes), 6.66, 6.70(m-H-mes), 8.07(d, J = 8Hz, H(7,11)), 8.01(d, J=6.5Hz, H(8,10)), 7.09(m, 9-H), 7.26(d, J=6Hz, H(4)), 7.34(d, J=5Hz, H(5)), 1.5(s, N-Me); Fluorine n.m.r.,  $^{19}\text{F}\{^1\text{H}\}$ , ppm, -78,  $^{13}\text{C}\{^1\text{H}\}$ , ppm, 134.5(C2), 124(C4), 125(C5), 125.3(C7,11), 129.2(C8,10), 134(C6), 42 (Me Gr.); Analysis for cis-[Au(mes)<sub>2</sub>(MeeaiMe)](OTf), **1b**,  $[\text{C}_{30}\text{H}_{34}\text{N}_4\text{Au}](\text{SO}_3\text{F}_3)$ , Calc(found): C, 45.94 (45.8), H, 4.3 (4.4), N, 7.1(7.1); IR  $\nu(\text{N}=\text{N})$  1360  $\nu(\text{C}=\text{N})$  1590  $\nu(\text{mes})$  1586(w), 849(m,Br),  $\nu(\text{OTf})$  1260(br), ES/MS, 784  $[\text{M}^+]$ , 634  $[\text{M-OTf}]$ ; Proton n.m.r.,  $^1\text{H}$ , ppm, 2.1(o-Mes), 2.2(p-Mes), 6.6, 6.7(m-H-mes), 8.0(d, J = 8Hz, H(7,11)), 8.1(d, J=6Hz, H(8,10)), 7.2(d, J=6Hz, H(4)), 7.3(d, J=5Hz, H(5)), 1.5(s, N-Me); Fluorine n.m.r.,  $^{19}\text{F}\{^1\text{H}\}$ , ppm, -78,  $^{13}\text{C}\{^1\text{H}\}$ , ppm, 134 (C2), 124(C4), 125(C5), 125 (C7,11), 129 (C8,10), 134(C6), 44 (Me Gr.); Analysis for cis-[Au(mes)<sub>2</sub>(Claaime)](OTf), **1c**,  $[\text{C}_{29}\text{H}_{31}\text{N}_4\text{AuCl}](\text{SO}_3\text{F}_3)$ , Calc(found): C, 43.4 (43.5), H, 3.9 (4.0), N, 6.96(7.0); IR  $\nu(\text{N}=\text{N})$  1370  $\nu(\text{C}=\text{N})$  1590  $\nu(\text{mes})$  1589(w), 849(m,Br),  $\nu(\text{OTf})$  1260(br), ES/MS, 804.5  $[\text{M}^+]$ , 654.5  $[\text{M-OTf}]$ ; Proton n.m.r.,  $^1\text{H}$ , ppm, 2.17(o-Mes), 2.29(p-Mes), 6.66, 6.7(m-H-mes), 8.0(d, J = 8Hz, H(7,11)), 8.0(d, J=6Hz, H(8,10)), 7.2(d, J=6Hz, H(4)), 7.34(d, J=5Hz, H(5)), 1.5(s, N-Me); Fluorine n.m.r.,  $^{19}\text{F}\{^1\text{H}\}$ , ppm, -78,  $^{13}\text{C}\{^1\text{H}\}$ , ppm, 134 (C2), 124(C4), 125(C5), 125.3(C7,11), 129 (C8,10), 134(C6), 46 (Me Gr.); Analysis for cis-[Au(mes)<sub>2</sub>(HaaiEt)](OTf), **1d**,  $[\text{C}_{30}\text{H}_{34}\text{N}_4\text{Au}](\text{SO}_3\text{F}_3)$ , Calc(found): C, 45.94 (45.8), H, 4.3 (4.4), N, 7.1(7.1); IR  $\nu(\text{N}=\text{N})$  1360  $\nu(\text{C}=\text{N})$  1590  $\nu(\text{mes})$  1586(w), 849(m,Br), ES/MS, 784  $[\text{M}^+]$ , 634  $[\text{M-OTf}]$ ; Proton n.m.r.,  $^1\text{H}$ , ppm, 2.1(o-Mes), 2.2(p-Mes), 6.6, 6.7(m-H-mes), 8.0(d, J = 8Hz, H(7,11)), 8.1(d, J=6Hz, H(8,10)), 7.9(m, 9-H), 7.2(d, J=6Hz, H(4)), 7.3(d, J=5Hz, H(5)), 1.5(s, N-Me); Fluorine n.m.r.,  $^{19}\text{F}\{^1\text{H}\}$ , ppm, -78,  $^{13}\text{C}\{^1\text{H}\}$ , ppm, 134 (C2), 124(C4), 125(C5), 125 (C7,11), 129 (C8,10), 134(C6), 50,44 (Et Gr.); Analysis for cis-[Au(mes)<sub>2</sub>(MeeaiEt)](OTf), **1e**,  $[\text{C}_{31}\text{H}_{36}\text{N}_4\text{Au}](\text{SO}_3\text{F}_3)$ , Calc(found): C, 46.64 (46.8), H, 4.5 (4.4), N, 7.0(7.0); IR  $\nu(\text{N}=\text{N})$  1350  $\nu(\text{C}=\text{N})$  1599  $\nu(\text{mes})$  1586(w), 849(m,Br),  $\nu(\text{OTf})$  1260(br), ES/MS, 798  $[\text{M}^+]$ , 648  $[\text{M-OTf}]$ ; Proton n.m.r.,  $^1\text{H}$ , ppm, 2.18(o-

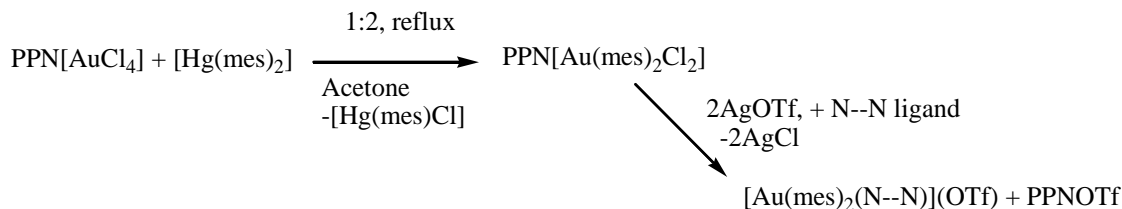
Mes), 2.27(p-Mes), 6.61, 6.71(m-H-mes), 8.0(d, J = 7Hz, H(7,11)), 8.1(d, J=6Hz, H(8,10)), 7.2(d, J=6Hz, H(4)), 7.3(d, J=5Hz, H(5)), 1.5(s, N-Me); Fluorine n.m.r.,  $^{19}\text{F}\{^1\text{H}\}$ , ppm, -78,  $^{13}\text{C}\{^1\text{H}\}$ , ppm, 134 (C2), 124.5(C4), 125(C5), 125 (C7,11), 129.7 (C8,10), 134(C6), 44,49 (Et Gr.); Analysis for cis-[Au(mes)<sub>2</sub>(ClaaiEt)](OTf), **1f**, [C<sub>30</sub>H<sub>33</sub>N<sub>4</sub>AuCl](SO<sub>3</sub>F<sub>3</sub>), Calc(found): C, 43.94 (43.8), H, 4.0 (4.0), N, 6.8(6.9); IR  $\nu(\text{N}=\text{N})$  1360  $\nu(\text{C}=\text{N})$  1599  $\nu(\text{mes})$  1589(w), 859(m,Br),  $\nu(\text{OTf})$  1260(br), ES/MS, 818.5 [M<sup>+</sup>], 6668.5 [M-OTf]; Proton n.m.r.,  $^1\text{H}$ , ppm, 2.1(o-Mes), 2.2(p-Mes), 6.6, 6.7(m-H-mes), 8.0(d, J = 8Hz, H(7,11)), 8.1(d, J=6Hz, H(8,10)), 7.2(d, J=6Hz, H(4)), 7.3(d, J=5Hz, H(5)), 1.5(s, N-Me); Fluorine n.m.r.,  $^{19}\text{F}\{^1\text{H}\}$ , ppm, -78,  $^{13}\text{C}\{^1\text{H}\}$ , ppm, 134 (C2), 124(C4), 125.5(C5), 125 (C7,11), 129.6 (C8,10), 134(C6), 44,49 (Et Gr.); Analysis for cis-[Au(mes)<sub>2</sub>(HaaiBz)](OTf), **1g**, [C<sub>35</sub>H<sub>36</sub>N<sub>4</sub>Au](SO<sub>3</sub>F<sub>3</sub>), Calc(found): C, 49.64 (49.8), H, 4.3 (4.24), N, 6.6(6.5); IR  $\nu(\text{N}=\text{N})$  1366  $\nu(\text{C}=\text{N})$  1596  $\nu(\text{mes})$  1586(w), 849(m,Br),  $\nu(\text{OTf})$  1267(br), ES/MS, 846 [M<sup>+</sup>], 696 [M-OTf]; Proton n.m.r.,  $^1\text{H}$ , ppm, 2.1(o-Mes), 2.2(p-Mes), 6.66, 6.7(m-H-mes), 8.0(d, J = 7Hz, H(7,11)), 8.1(d, J=5Hz, H(8,10)), 7.9(m, 9-H), 7.2(d, J=6Hz, H(4)), 7.3(d, J=5Hz, H(5)), 4.5, 7.1-7.3(s, N-Bz); Fluorine n.m.r.,  $^{19}\text{F}\{^1\text{H}\}$ , ppm, -78,  $^{13}\text{C}\{^1\text{H}\}$ , ppm, 134 (C2), 124(C4), 125(C5), 125.5 (C7,11), 129 (C8,10), 134(C6), 44,130-132 (Bz Gr.); Analysis for cis-[Au(mes)<sub>2</sub>(MeaaiBz)](OTf), **1h**, [C<sub>36</sub>H<sub>38</sub>N<sub>4</sub>Au](SO<sub>3</sub>F<sub>3</sub>), Calc(found): C, 50.24 (50.8), H, 4.3 (4.4), N, 6.5(6.4); IR  $\nu(\text{N}=\text{N})$  1366  $\nu(\text{C}=\text{N})$  1597  $\nu(\text{mes})$  1586(w), 849(m,Br),  $\nu(\text{OTf})$  1266(br), ES/MS, 864 [M<sup>+</sup>], 710 [M-OTf]; Proton n.m.r.,  $^1\text{H}$ , ppm, 2.1(o-Mes), 2.2(p-Mes), 6.6, 6.7(m-H-mes), 8.0(d, J =8Hz, H(7,11)), 8.1(d, J=6Hz, H(8,10)), 7.2(d, J=6Hz, H(4)), 7.3(d, J=5Hz, H(5)), 4.5, 7.1-7.3(s, N-Bz); Fluorine n.m.r.,  $^{19}\text{F}\{^1\text{H}\}$ , ppm, -78,  $^{13}\text{C}\{^1\text{H}\}$ , ppm, 134.5 (C2),

124(C4), 125(C5), 125 (C7,11), 129.6 (C8,10), 134(C6), 44,130-132(Bz Gr.); Analysis for cis-[Au(mes)<sub>2</sub>(ClaaiBz)](OTf), **1i**, [C<sub>35</sub>H<sub>35</sub>N<sub>4</sub>Au](SO<sub>3</sub>F<sub>3</sub>), Calc(found): C, 47.7 (47.8), H, 3.9 (3.8), N, 6.31(6.2); IR  $\nu(\text{N}=\text{N})$  1365  $\nu(\text{C}=\text{N})$  1597  $\nu(\text{mes})$  1586(w), 849(m,Br),  $\nu(\text{OTf})$  1260(br), ES/MS, 880.5 [M<sup>+</sup>], 730.5 [M-OTf]; Proton n.m.r.,  $^1\text{H}$ , ppm, 2.11(o-Mes), 2.22(p-Mes), 6.62, 6.7(m-H-mes), 8.0(d, J = 8Hz, H(7,11)), 8.1(d, J=6Hz, H(8,10)), 7.9(m, 9-H), 7.2(d, J=6Hz, H(4)), 7.3(d, J=5Hz, H(5)), Fluorine n.m.r.,  $^{19}\text{F}\{^1\text{H}\}$ , ppm, -78,  $^{13}\text{C}\{^1\text{H}\}$ , ppm, 134 (C2), 124.5(C4), 125(C5), 125 (C7,11), 129 (C8,10), 134(C6), 44, 130-133 (Bz Gr.); Analysis for cis-[Au(mes)<sub>2</sub>(dppm)](OTf), **2**, [C<sub>44</sub>H<sub>48</sub>Au](SO<sub>3</sub>F<sub>3</sub>), Calc(found): C, 54.1 (54.0), H, 4.6 (4.4), IR  $\nu(\text{C}=\text{C})$  1590  $\nu(\text{mes})$  1586(w), 849(m,Br),  $\nu(\text{OTf})$  1260(br), FAB, 819[M<sup>+</sup>], Proton n.m.r.,  $^1\text{H}$ , ppm, 2.1(o-Mes), 2.2(p-Mes), 6.6, 6.7(m-H-mes), 7.1-7.3(m, H(dppm)), 2.5;  $^{31}\text{P}\{^1\text{H}\}$ , ppm, -25.5, Fluorine n.m.r.,  $^{19}\text{F}\{^1\text{H}\}$ , ppm, -78,  $^{13}\text{C}\{^1\text{H}\}$ , ppm, 130.4-132.6, 43, (C-dppm), 126.6 (m-H-mes); Analysis for cis-[Au(mes)<sub>2</sub>(dppe)](OTf), **3**, [C<sub>45</sub>H<sub>50</sub>Au](SO<sub>3</sub>F<sub>3</sub>), Calc(found): C, 56.1 (56.0), H, 5.2 (5.4), IR  $\nu(\text{C}=\text{C})$  1630  $\nu(\text{mes})$  1586(w), 849(m,Br),  $\nu(\text{OTf})$  1260(br), FAB, 832[39%,M<sup>+</sup>], Proton n.m.r.,  $^1\text{H}$ , ppm, 2.1(o-Mes), 2.2(p-Mes), 6.3, 6.6(m-H-mes), 2.5; 7.1-7.3(m, H(dppe)),  $^{31}\text{P}\{^1\text{H}\}$ , ppm, 45.1, Fluorine n.m.r.,  $^{19}\text{F}\{^1\text{H}\}$ , ppm, -78,  $^{13}\text{C}\{^1\text{H}\}$ , ppm, 130.9-132.6, 40, (C-dppe), 126.6 (m-H-mes); Analysis for cis-[Au(mes)<sub>2</sub>(dppa)](OTf), **4** [C<sub>43</sub>H<sub>47</sub>Au] (SO<sub>3</sub>F<sub>3</sub>), Calc(found): C, 54.1 (54.0), H, 4.6 (4.4), IR  $\nu(\text{C}=\text{C})$  1600  $\nu(\text{mes})$  1596(w), 859(m,Br),  $\nu(\text{OTf})$  1250(br), FAB, 820[M<sup>+</sup>], Proton n.m.r.,  $^1\text{H}$ , ppm, 2.1(o-Mes), 2.2(p-Mes), 6.3 (m-H-mes), 2.5; 7.1-7.3(m, H(dppa)), Fluorine n.m.r.,  $^{19}\text{F}\{^1\text{H}\}$ , ppm, -78,  $^{13}\text{C}\{^1\text{H}\}$ , ppm, 130.9-132.6, 43, (C-dppa), 124.6 (m-H-mes).

## Results and Discussion

### 3.1. Synthesis and formulation

### Scheme 1

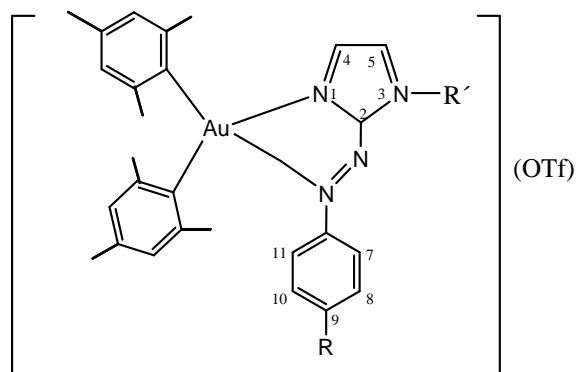


N--N = RaaiR' (**1a,1b,1c,1d,1e,1f, 1g,1h,1i**); dppm(**2**), dppe(**3**), dppa(**4**)

R' = Me, R=H(**1a**), Me(**1b**), Cl(**1c**)

R' = Et, R=H(**1d**), Me(**1e**), Cl(**1f**)

R' = Bz, R=H(**1g**), Me(**1h**), Cl(**1i**)



The reaction in refluxing acetone of PPN[AuCl<sub>4</sub>] with Hg(mes)<sub>2</sub> in a molar ratio 1:2 for 10 h leads to the formation of *cis*-PPN[Au(mes)<sub>2</sub>Cl<sub>2</sub>] together with [Hg(mes)Cl] in high yield. Both compounds are easily separated and purified by fractional crystallization. Attempts to substitute more chloride anions by mesityl groups following the method described in Scheme 1 failed. Reaction of *cis*-PPN[Au(mes)<sub>2</sub>Cl<sub>2</sub>] followed by arylazoimidazole in dichloromethane medium leads to [Au(mes)<sub>2</sub>(RaaiR)], (**1a-1i**), [RaaiR' = *p*-R-C<sub>6</sub>H<sub>4</sub>-N=N-C<sub>3</sub>H<sub>2</sub>-NN-1-R', abbreviated as N,N'-chelator, where N(imidazole) and N(azo) represent N and N', respectively; R = H, Me, Cl and R' = Me, CH<sub>2</sub>CH<sub>3</sub>, CH<sub>2</sub>Ph, OSO<sub>2</sub>CF<sub>3</sub> is the triflate anion]. All the complexes are supported by elemental analysis and well characterised by IR, multinuclear NMR (<sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P, <sup>19</sup>F, COSY, HMQC) and ESI mass spectrophotometrically

### 3.2. Spectral study

The IR spectra show absorptions from the mesityl ligand for all the compounds. The intense stretching at 1365-1370 and 1570-1580 cm<sup>-1</sup> with concomitant loss of  $\nu(\text{Au-Cl})$  at 260-298 cm<sup>-1</sup>. They are assigned to  $\nu(\text{N=N})$  and  $\nu(\text{C=N})$ , respectively. The IR spectra of the starting material *cis*-PPN[Au(mes)<sub>2</sub>Cl<sub>2</sub>] (**1**) shows two absorptions at 291 (s) and 278 (s) that can be assigned to two active bands (Au-Cl) (a<sub>1</sub>, b<sub>1</sub>) of the *cis*-isomer (C<sub>2v</sub> symmetry).

Their <sup>1</sup>H-NMR spectra are as expected showing three signals due to the mesityl ligand (protons from the *ortho*- and *para*-methyl groups and protons in *meta*). For the phosphine complexes (**2** and **3**) the assigned signal for *m*-H of one mesityl group is observed as a doublet (<sup>5</sup>J<sub>P-H</sub>=3.9 Hz) due to the coupling with the phosphine in *trans*. All these data is consistent with the proposal of square-planar complexes being the *cis* isomers. The signals assigned to the mesityl ligand in the <sup>1</sup>H-NMR spectra of the neutral compounds are very similar to those found for **1**.

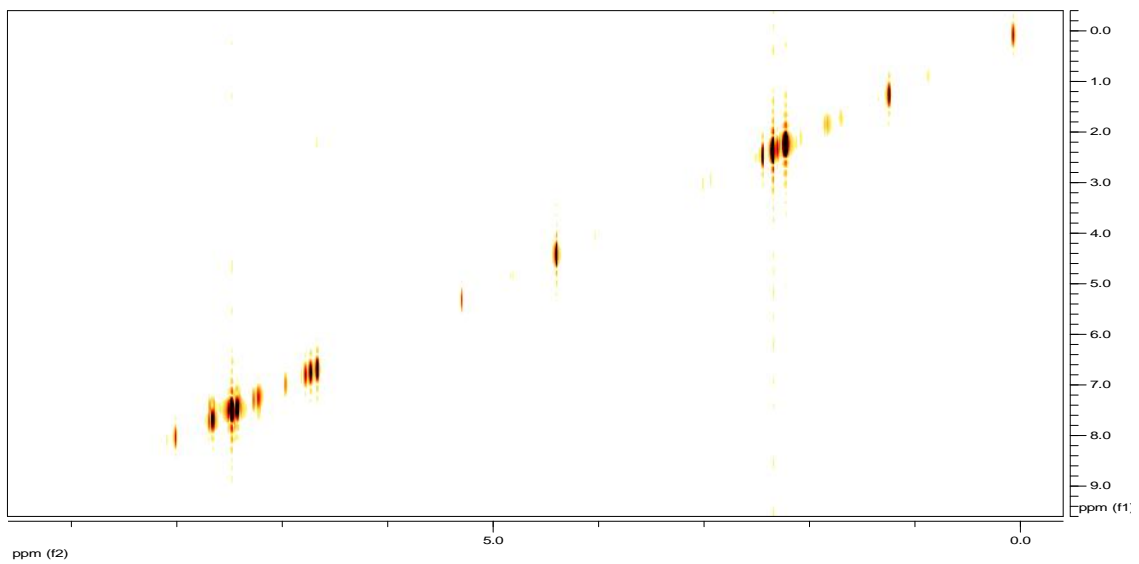
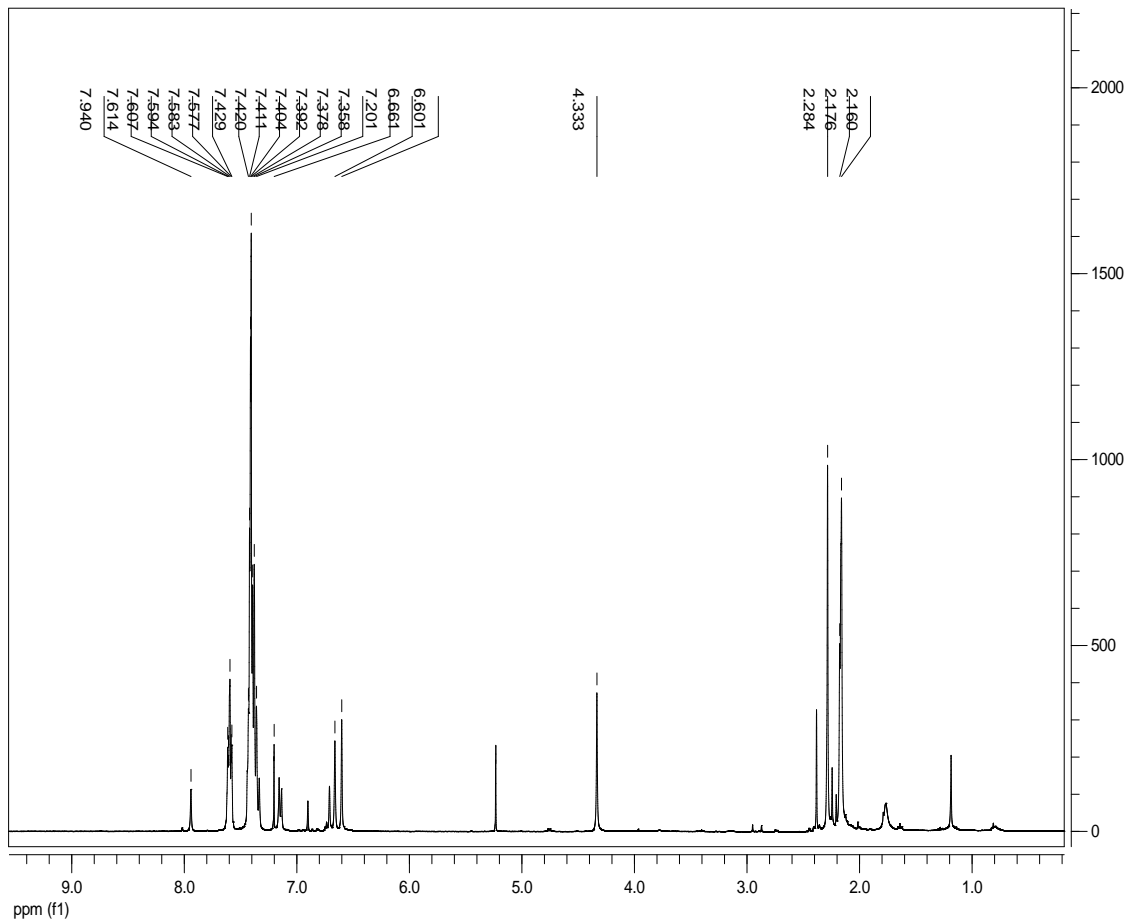
The <sup>31</sup>P{<sup>1</sup>H}-NMR of the compounds containing bidentate phosphines shows a singlet but at very different chemical shifts. The ligand show a singlet at -22.2(dppm), -12.2(dppe) and the parent dichloro gold complexes show a singlet at 24.7(Au<sub>2</sub>dppmCl<sub>2</sub>), 32(Au<sub>2</sub>dppeCl<sub>2</sub>). But due to the presence of mesityl group in the case of **3** (L=L=dppe) the signal appears at 45.1 ppm (consistent with two phosphorus atoms coordinated to a gold(III) centre). For **2** (L=L=dppm) the resonance is highly shielded (-25.5 ppm) and explained on the basis of the constrain imposed on the four-membered phosphorus chelate ring as described for other metallic complexes [27].

Fluorine n.m.r., <sup>19</sup>F {<sup>1</sup>H}, (measured in CDCl<sub>3</sub>) is informative of the present series of complexes. All shows a singlet peak at -78 due to the presence of triflate ion.

The <sup>13</sup>C (H)NMR spectrum provides direct information about the carbon skeleton of the molecule. Assignment of different resonant peaks to respective carbon atoms are done for all complexes. Considering one arylazoimidazole moieties there are different carbon atoms in the molecule which gives different peaks in the <sup>13</sup>C (H)NMR spectrum. Carbon atoms neighbouring to the nitrogen atom shifted to downfield due to an increased electron density resulting from the presence of electronegative nitrogen atom and *pi* electron delocalization in the magnetic environment. The non-protonated carbon atoms at C(2) and C(6) of the arylazoimidazole moiety is shifted farthest downfield in the spectrum effected by the magnetic interaction of two bulky phenyl rings environment and the methyl, ethyl, benzyl substituted imidazole rings and the *pi* electron delocalization on the =N-CC=N- and =N-C-C=C-C-.

The COSY spectrum reveals the <sup>1</sup>H-<sup>1</sup>H coupling interactions in the molecule. The cross peaks along both the sides of the diagonal identify the nuclei that are coupled to each other. On the contrary, the protons that are decoupled from the adjacent ones due to the lack of  $\alpha$ -protons will show no correlation in the spectrum. Extending horizontal and vertical lines from  $\delta = 7.32$  ppm [C(4)H] and 7.68 ppm [C(5)H] encounter cross peaks at  $\delta = 7.12$  ppm and 7.23 ppm, where the C(7)H and C(11)H resonances are merged into multiplets along with the phenyl ring proton resonances. The comperative weaker coupling interactions of mesitylene ortho and para methyl protons and the meta proton with the far apart positioned C(4)H and C(5)H protons of the imidazole moiety are shown by the poorly resolved cross peaks at  $\delta = 7.32$  ppm and 7.83 ppm.

The <sup>1</sup>H-<sup>13</sup>C heteronuclear multiple-quantum coherence (HMQC) spectrum provides information regarding the interaction between the protons and the carbon atoms to which they are directly attached. In the present complexes, the absence of any contours at  $\delta = 147.12$ , 160.76, 155.67 ppm and 157.68 ppm assign them to the C(2), C(6), C(ipso-mesityl) and C(ortho,para) carbon atoms respectively. This is because, they belong to the non-protonated carbon atoms on the imidazole, phenyl and mesityl rings. So they are unable to show any direct <sup>1</sup>H-<sup>13</sup>C heteronuclear multiple-quantum coherence.



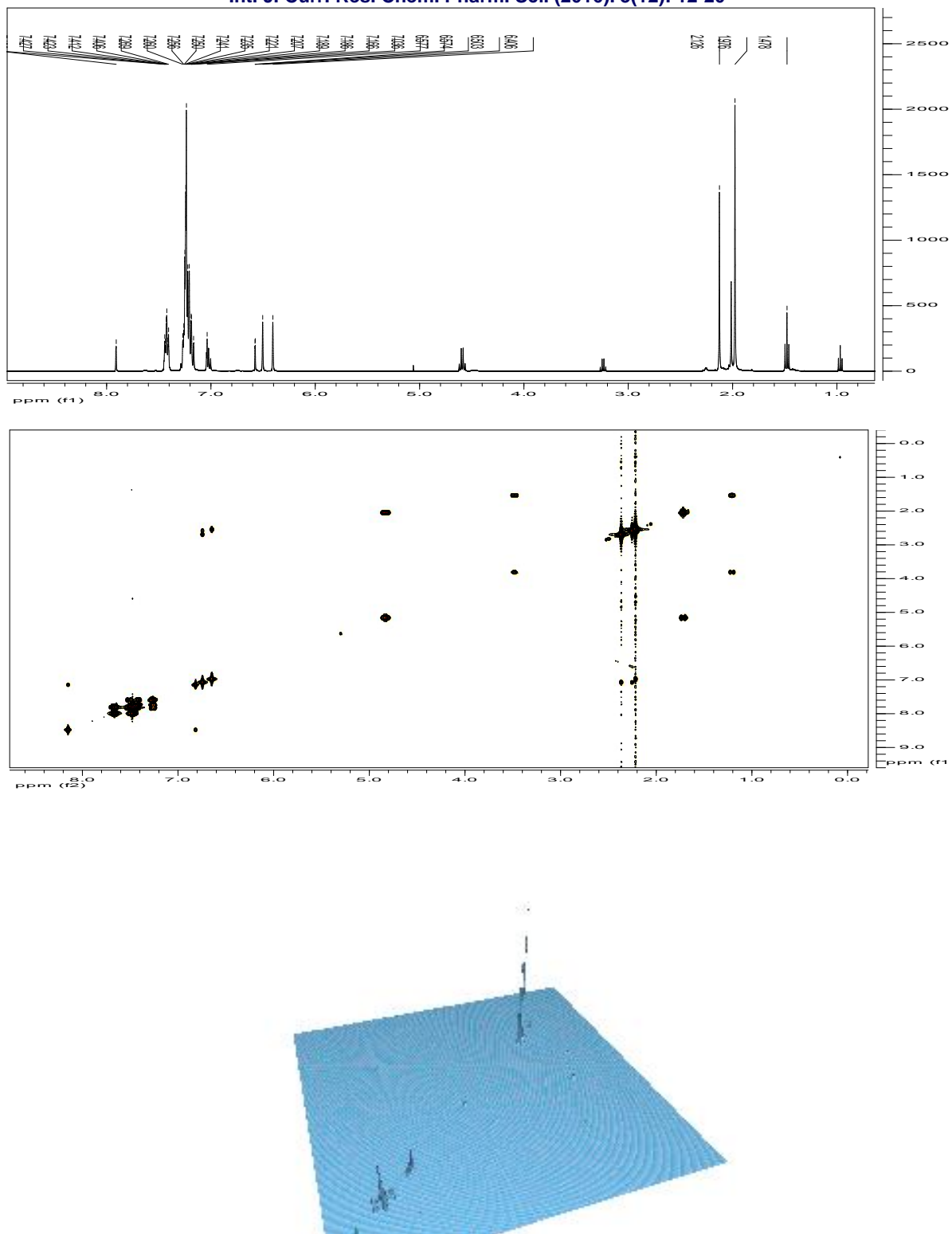


FIGURE 2. Complete  $^1\text{H}$  NMR and  $^{13}\text{C}$  (H) NMR of complex (2b).

## 4. Conclusions

This work describes the isolation of  $[\text{Au}(\text{mes})_2(\text{RaaiR}')](\text{OTf})$  and their spectral and elemental characterisation.  $^{19}\text{F}$   $\{^1\text{H}\}$  NMR as well as  $^{31}\text{P}$   $\{^1\text{H}\}$  NMR is helpful to assign the solution structure of the complexes. In the  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of the present complexes, as well as the contour peaks in the  $^1\text{H}$ - $^{13}\text{C}$  HMQC spectrum in the present complexes, helps to assign the dimensional relationship among proton proton and proton carbon.

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