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Gold (III)-(Chloro)-Mono or Bis-(Triphenylphosphine) - (Naphthyl-Azo-Imidazole/ Benzimidazole/Pyridine) Complexes: Synthesis, Spectroscopic Study and Cyclic Voltammetric Study

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ABSTRACT

Reaction of Gold(III) tetrachloride H[Au(Cl_4)] with NaaiR′ in Acetone medium following ligand (Triphenyl phosphine, PPh_3) addition leads to [Au(PPh_3)$_2$(NaaiR′)] and [Au(PPh_3)(Cl)(NaaiR′)], [NaaiR′ = naphthyl-azo imidazole /benzimidazole /pyridine = $C_{10}H_4$-N=N- / C_3H_2-NN-1-R′, (R imidazole) / C_7H_4-NN-1-H (Benzimidazole), / C_3H_4-N-(Pyridine), abbreviated as N,N′-chelator, where N(imidazole) and N(azo) represent N and N′, respectively; R′ = H(*a*), Me (*b*), PPh_3 = Triphenyl phosphine, PPh_3]. The ^{1}H NMR spectral measurements suggest the molecular structure of bis chelated complex with the protons at the aromatic region and naphthyl protons at higher ∂ value. The voltammogram also shows a good result and support the complex formation.

Keywords: Gold (III), chloro-triphenylphosphine Naphthylazoimidazole, CV, NMR, IR, ESIMS.

INTRODUCTION

Running years have witnessed a great deal of interest in the synthesis of the complexes of gold with α-diimine type of ligands because of their photochemical, catalytic properties (Chung-Chin, *et al.*, 2014; Messori *et al.*, 2014*;* Naeem *et al.*, 2014; Bertrand *et al.*, 2014**)**, energy conversion and ability to serve as building blocks in supramolecular arrays (Byabartta *et al.*, 2014; Byabartta, 2014; Byabartta, 2014; Byabartta *et al.*, 2001; Byabartta *et al.*, 2003). Today in vivo biochemistry of gold remains enigmatic, mainly due to a paucity of adequate models and an inadequate understanding of the reactivity of gold **(**Sung *et al.*, 2013; Holmberg *et al*, 2013*;*, *et al.*, 2013*;* Abbehausen *et al.*, 2013*;* Huang *et al*, 2013*;* Li *et al*,

2013*;* Ciabatti *et al., 2013*; Robilotto *et al.,* 2013). Moreover, as gold is not a metal naturally used in metabolism, it is believed that its chemistry in vivo differs from other transition metals such as iron and copper, which are carefully transported and stored by enzymatic processes. The biochemistry of gold with D-penicillamine, gluthadione, thiomalic acid, 2,3-dimercaptopropanol, and albumin has been studied (Shi Yi *et al*., 2013; Kraus *et al,* 2013*;* Zhou *et al,* 2013*;* Wilson *et al*, 2013; Cauteruccio *et al.. 2013.* Gutiérrez A, Bernal J, Villacampa M. D, *et al*, 2013; Shichibu Y and Konishi K. 2013. Ou *et al.,* 2013**)**. The reactivity of gold occurs though the thiolate function of these biological molecules and leads to the formation of gold (I) thiolates, also called chrysotherapy agents. These complexes are efficient against rheumatoid arthrisis and even HIV and are commercialized under different trade names such as Myochrysine, Solganol, Krysolgan, and Allochrysine. Other types of gold complexes used in medicinal chemistry are gold (I) mono- or bis-phosphines. They can bind to DNA via the guanine and cytosine bases and act as antitumor agents against L1210 leukemia and M5076 reticulum cell sarcoma. In 1972, Sutton synthesized a gold complex with a thiolate and a phosphine ligand: the 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-pyranosato-*S*-(triethylphosphine)gold(I) compound also known by the trade name Auranofin. It became one of the most promising gold complexes in medicinal chemistry, with a great potency against rheumatoid arthritis and cancer cells such as P388 leukemia and B16 (Shi *et al.,* 2013; Kraus *et al,* 2013; Zhou *et al.,* 2013; Wilson *et al*, 2013; Cauteruccio *et al.,* 2013; Gutiérrez *et al.,* 2013*;* Shichibu *et al.,* 2013**)**. A small number of scattered observations in the early structural chemistry of gold(I) complexes has grown into a wealth of reports on related phenomena in the last two decades, which finally provided a clear pattern of the conditions under which direct interactions between closed-shell gold(I) centers can contribute significantly to the stability of molecular and multidimensional structures (Gao *et al.,* 2012; Rodríguez *et al*., 2012; Smetana *et al.,* 2012; Koshevoy *et al.,* 2012; Katari *et al.,* 2012; Overton, 2012; Wang *et al.,* 2012; Zhou Yu *et al.,* 2012; *et al.,* 2012; Cabeza *et al.,* 2012; **,**Chai Pi and Corbett, 2012**)**. The underlying "aurophilic" bonding has been analyzed in theoretical studies (Lim *et al,* 2013*;* Celik *et al,* 2013; Tsipis *et al*, 2013; Latouche *et al.,* 2012; Cervellera, 2012; Dolzhnikov *et al.,* 2012*;* Miao *et al*., 2012). Syntheses of hetero-*tris*-chelates, $[Ru(bpy)_n(RaaiR^{/})_{3-n}](ClO_4)_2$ [bpy = 2,2′-bipyridine; n = 1, n = 2) containing labile reaction centres are reported from Prof. Sinha´s laboratory . Prof. A Chakravorty has unfolded this ligands rhenium chemistry. But the gold chemistry with multinuclear NMR spectroscopy of this ligand system is totally unexplored. In this paper, we examine the reaction of $NaaiR^{/}$ on gold(III) bis-triphenylphosphine derivatives and the products are isolated, $[Au(PPh_3)_2(NaaiR^{/})]$ and $[Au(PPh_3)(Cl)(NaaiR^{/})]$, [$NaaiR^{/}$ = naphthyl-azo imidazole /benzimidazole /pyridine = $C_{10}H_4$-N=N- / C_3H_2-NN-1-$R^{/}$, (R imidazole) / C_7H_4-NN-1-H (Benzimidazole), / C_3H_4-N-(Pyridine), abbreviated as N,$N^{/}$-chelator, where N(imidazole) and N(azo) represent N and $N^{/}$, respectively; $R^{/}$ = H(*a*), Me (*b*), PPh_3 = Triphenyl phosphine, PPh_3]. The complexes are well charecterised by i.r., ^{1}H n.m.r., ^{13}C nmr and mass spectrometry.

MATERIALS AND METHODS

Material and Instrumentation

Published methods were used to prepare Naphthyl-azo-imidazole /benzimidazole/ pyridine (Byabartta *et al.,* 2014; Byabartta, 2014; Byabartta, 2014; Byabartta *et al.,* 2001; Byabartta *et al*., 2003). All other chemicals 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 JASCO 420 spectrophotometer (using KBr disks, 4000-200 cm^{-1}). The ^{1}H nmr spectra in $CDCl_3$ were obtained on a Bruker 500 MHz FT n.m.r spectrometer using $SiMe_4$ as internal reference, $CFCl_3$ (external ^{19}F). Solution electrical conductivities were measured using a Systronics 304 conductivity meter with solute concentration ~10^{-3} M in acetonitrile. Mass spectra were

recorded on VG Autospec ESI-mass spectrometry. Electrochemical work was carried out using an EG & G PARC Versastat computer controlled 250 electrochemical system. All experiments were performed under a N_2 atmosphere at 298K using a Pt-disk milli working electrode at a scan rate of 50 mVs^{-1}. All results were referenced to a saturated calomel electrode (SCE).

Preparation of the complexes

Synthesis of different gold- pph$_3$ compound

Synthesis of the compound 1.

In a 100ml rb 0.07112 g Phenyl azo benzimidazole (PABEN) was taken and 25ml of methanol was added. The above ligand was fully soluble in methanol and the colour was pale yellow. Now 0.1078 g of $HAuCl_4$ i.e. 0.00032 mole was added into this solution. It was stirred and after few minutes 0.1678g i.e. 2 eqv of triphenyl phosphine (PPh_3) was added into the mixture. Now it was refluxed for 24 hours and the colour change was observed. It was a white colour solution. After the completion of the reaction it was filtered & filtrate was collected for crystal tube setting and for another characterization analysis of the compound.

Characterisation of the compound 1**:** CHN calculation of the above compound [$C_{31}H_{25}N_4P_2Au$], gives Calc(found): C, 52.26 (52.2), H, 3.53 (3.5), N, 7.86(7.8); IR Spectroscopic data, ν(N=N) 1370 ν(C=N) 1590, ESI/MS Spectroscopic data, 712.4 [M^+], Proton n.m.r.Spectroscopic data, ^{1}H, ppm, 8.09(d, J = 8Hz, H(7,11)), 8.06(d, J=6.5Hz, H(8,10)), 7.01(m, 9-H), 7.20(d, J=6Hz, H(4)), 7.31(d, J=5Hz, H(5)), UV-Vis Spectroscopic data, (λ nm), 400(6500), 280(8160), 282(8200), 295(600),(sh); Electrochemistry or Cyclic Voltammetric data ($E_{1/2}$ (V) (E_p(mV) [Solvent MeCN, Supporting Electrolyte, Bu_4NClO_4 (0.1 M), scan rate 50 mVs^{-1}, Pt disk working electrode, Pt wire auxiliary electrode, referance electrode SCE at 298 K] Ligand reduction -0.56 (80), Matal oxidation 0.33 (90).

Synthesis of the compound 2

In a 100ml rb 0.1251g 1-methyl napthyl azo imidazole (MeNAIM) was taken and 25ml of methanol was added. The above ligand was fully soluble in methanol and the colour was orange. Now 0.1791g of $HAuCl_4$ i.e. 0.00053 mole was added into this solution. It was stirred and after few minutes 0.1390g i.e. 1 eqv of triphenyl phosphine (PPh_3) was added into the mixture. Now it was refluxed for 24 hours and the colour change was observed. It was a golden yellow colour solution. After the completion of the reaction it was filtered & filtrate was collected for crystal tube setting and for another characterization analysis of the compound.

Characterisation of the compound 2**:** CHN calculation of the above compound [$C_{32}H_{27}N_4PClAu$], gives Calc(found): C, 52.58 (52.5), H, 3.72 (3.7), N, 7.66 (7.6); IR Spectroscopic data, ν(N=N) 1370 ν(C=N) 1590, ESI/MS Spectroscopic data, 730.95 [M^+], Proton n.m.r.Spectroscopic data, ^{1}H, ppm, 8.0(d, J = 8Hz, H(7,11)), 8.1(d, J=6.5Hz, H(8,10)), 7.9(m, 9-H), 7.26(d, J=6Hz, H(4)), 7.34(d, J=5Hz, H(5)), UV-Vis Spectroscopic data, (λ nm), 444(7500), 283(8160), 280(8200); Electrochemistry or Cyclic Voltammetric data ($E_{1/2}$ (V) (E_p(mV) [Solvent MeCN, Supporting Electrolyte, Bu_4NClO_4 (0.1 M), scan rate 50 mVs^{-1}, Pt disk working electrode, Pt wire auxiliary electrode, referance electrode SCE at 298 K] Ligand reduction -0.416 (80), Matal oxidation 0.313 (80).

Synthesis of the compound 3

In a 100ml rb 0.1134g 1-methyl napthyl azo imidazole (MeNAIM) was taken and 25ml of methanol was added. The above ligand was fully soluble in methanol and the colour was orange. Now 0.1623 g of $HAuCl_4$ i.e. 0.00048 mole was added into this solution. It was stirred and after few minutes 0.2518g i.e. 2 eqv of triphenyl phosphine (PPh_3) was added into

the mixture. Now it was refluxed for 24 hours and the colour change was observed. It was a golden yellow colour solution. After the completion of the reaction it was filtered & filtrate was collected for crystal tube setting and for another characterization analysis of the compound.

***Characterisation of the compound 3*:** CHN calculation of the above compound [$C_{50}H_{42}N_4P_2Au$], gives Calc(found): C 62.70(62.7), H, 4.41 (4.4), N, 5.84(5.8); IR Spectroscopic data, ν(N=N) 1370 ν(C=N) 1590, ESI/MS Spectroscopic data,957.7 [M^+], Proton n.m.r.Spectroscopic data, ^{1}H, ppm, 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); UV-Vis Spectroscopic data, (λ nm), 400(4500), 280(8160), 295(600),(sh); Electrochemistry or Cyclic Voltammetric data ($E_{1/2}$ (V) (E_p(mV) [Solvent MeCN, Supporting Electrolyte, Bu_4NClO_4 (0.1 M), scan rate 50 mVs^{-1}, Pt disk working electrode, Pt wire auxiliary electrode, referance electrode SCE at 298 K Ligand reduction -0.522 (60), Matal oxidation 0.39 (100).

Synthesis of the compound 4

In a 100 ml rb 0.1117g 1-methyl phenyl azo imidazole (MePAIM) was taken and 25ml of methanol was added. The above ligand was fully soluble in methanol and the colour was light orange. Now 0.2035 g of $HAuCl_4$ i.e. 0.0006 mole was added into this solution. It was stirred and after few minutes 0.3147 g i.e. 2 eqv of triphenyl phosphine (PPh_3) was added into the mixture. Now it was refluxed for 24 hours and the colour change was observed. It was a golden yellow colour solution. After the completion of the reaction it was filtered & filtrate was collected for crystal tube setting and for another characterization analysis of the compound.

***Characterisation of the compound 4*:** CHN calculation of the above compound [$C_{46}H_{40}N_4P_2Au$], gives Calc(found): C, 60.86(60.8), H, 4.44 (4.5), N, 6.17 (6.1); IR Spectroscopic data, ν(N=N) 1370 ν(C=N) 1590, ESI/MS Spectroscopic data, 907.7 [M^+], Proton n.m.r.Spectroscopic data, ^{1}H, ppm, 8.27(d, J = 8Hz, H(7,11)), 8.11(d, J=6.5Hz, H(8,10)), 7.19(m, 9-H), 7.16(d, J=6Hz, H(4)), 7.14(d, J=5Hz, H(5)), 1.51(s, N-Me); UV-Vis Spectroscopic data, (λ nm), 441(6500), 280(8160), 286(8200), Electrochemistry or Cyclic Voltammetric data ($E_{1/2}$ (V) (E_p(mV) [Solvent MeCN, Supporting Electrolyte, Bu_4NClO_4 (0.1 M), scan rate 50 mVs^{-1}, Pt disk working electrode, Pt wire auxiliary electrode, referance electrode SCE at 298 K] Ligand reduction -0.516 (80), Matal oxidation 0.35 (100).

Synthesis of the compound 5

In a 100ml rb 0.0577 g 1-methyl phenyl azo imidazole (MePAIM) was taken and 25ml of methanol was added. The above ligand was fully soluble in methanol and the colour was light orange. Now 0.1052 g of $HAuCl_4$ i.e. 0.00031 mole was added into this solution. It was stirred and after few minutes 0.0813 g i.e.1 eqv of triphenyl phosphine (PPh_3) was added into the mixture. Now it was refluxed for 24 hours and the colour change was observed. It was a golden yellow colour solution. After the completion of the reaction it was filtered & filtrate was collected for crystal tube setting and for another characterization analysis of the compound.

Characterisation of the compound 5: CHN calculation of the above compound [$C_{28}H_{25}N_4Cl$ P Au], gives Calc(found): C, 49.39(49.3), H, 3.69 (4.0), N, 8.22 (8.23); IR Spectroscopic data, ν(N=N) 1370 ν(C=N) 1590, ESI/MS Spectroscopic data, 680.8 [M^+], Proton NMR Spectroscopic data, ^{1}H, ppm, 8.7(d, J = 8Hz, H(7,11)), 8.1(d, J=6.5Hz, H(8,10)), 7.9(m, 9-H), 7.6(d, J=6Hz, H(4)), 7.4(d, J=5Hz, H(5)), 1.5(s, N-Me); UV-Vis Spectroscopic data, (λ nm), 404(7500), 280(8160), 285(8200), 295(600),(sh); Electrochemistry or Cyclic Voltammetric data ($E_{1/2}$ (V) (E_p(mV) [Solvent MeCN, Supporting Electrolyte, Bu_4NClO_4

(0.1 M), scan rate 50 mVs^{-1}, Pt disk working electrode, Pt wire auxiliary electrode, referance electrode SCE at 298 K] Ligand reduction -0.516 (80), Matal oxidation 0.403 (100).

Synthesis of the compound 6

In a 100ml rb 0.499 g phenyl azo imidazole (PAIM) was taken and 25 ml of methanol was added. The above ligand was fully soluble in methanol and the colour was yellow. Now 0.0.1 g of $HAuCl_4$ i.e. 0.00029 moles was added into this solution. It was stirred and after few minutes 0.0761g i.e.1 eqv of triphenyl phosphine (PPh_3) was added into the mixture. Now it was refluxed for 24 hours and the colour change was observed. It was a golden yellow colour solution. After the completion of the reaction it was filtered & filtrate was collected for crystal tube setting and for another characterization analysis of the compound.

Characterisation of the compound 6: CHN calculation of the above compound [C_{27} H_{23} N_4 P Cl [Au], gives Calc(found): C, 48.62 (48.6), H, 3.47 (3.4), N, 8.40 (8.4); IR Spectroscopic data, ν(N=N) 1370 ν(C=N) 1590, ESI/MS Spectroscopic data, 666.86 [M^+], Proton NMR Spectroscopic data, ^{1}H, ppm, 8.07(d, J = 8Hz, H(7,11)), 8.1(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)), UV-Vis Spectroscopic data, (λ nm), 404(5500), 280(8160), 288(8200), 294(600),(sh); Electrochemistry or Cyclic Voltammetric data ($E_{1/2}$ (V) (E_p(mV) [Solvent MeCN, Supporting Electrolyte, Bu_4NClO_4 (0.1 M), scan rate 50 mVs^{-1}, Pt disk working electrode, Pt wire auxiliary electrode, referance electrode SCE at 298 K] Ligand reduction -0.526 (80), Matal oxidation 0.393 (70)

RESULTS AND DISCUSSION

Synthesis and Formulation

Reaction of Gold(III) tetrachloride H[Au(Cl_4)] with NaaiR´ in Acetone medium following ligand (Triphenyl phosphine, PPh_3) addition leads to [Au(PPh_3)$_2$(NaaiR$^/$)] and [Au(PPh_3)(Cl)(NaaiR$^/$)], [NaaiR$^/$ = naphthyl-azo imidazole /benzimidazole /pyridine = $C_{10}H_4$-N=N- / C_3H_2-NN-1-R$^/$, (R imidazole) / C_7H_4-NN-1-H (Benzimidazole), / C_3H_4-N- (Pyridine), abbreviated as N,N$^/$-chelator, where N(imidazole) and N(azo) represent N and N$^/$, respectively; R$^/$ = H(*a*), Me (*b*), PPh_3 = Triphenyl phosphine, PPh_3] were prepared by removing Cl, with NaaiR under stirring at 343-353 K in MeOH solution in poor yield (35-40%). The composition of the complexes is supported by microanalytical results. The orange complexes are soluble in common organic solvents viz. acetone, acetonitrile, chloroform, and dichloromethane but not soluble in H_2O, methanol, ethanol. The voltammogram also shows a small anodic peak at 0.400 V.

Spectral Studies

I.R. spectra of the complexes, show a 1:1 correspondence to the spectra of the chloro analogue, except the appearance of intense stretching at 1365-1370 and 1570-1580 cm^{-1} with concomitant loss of ν(Au-Cl) at 300-340 cm^{-1}. They are assigned to ν(N=N) and ν(C=N) appear at 1365-1380 and 1570-1600 cm^{-1}, respectively.

The ESI mass spectrum of a 1:1, MeCN: H_2O solution in the positive ion mode is structurally enlightening, since it displays a series of characteristic singly. Population of gas phase ions generated by ESI often closely reflects that in solution.

The electronic spectra of the complexes exhibit multiple high intense transitions in 450–250 nm. In free ligand, the intra-ligand charge transfer, n–p* and p–p*, appear at 370–380 and 250–260 nm, respectively. Low energy weak transition at 700–710 nm (Fig. 2) may be referred to d–d band. Gold(III)–azo-heterocycle and azide bridzed heterocycles show the MLCT transition involving d(Au) --- p* (Naphthylazoheterocycle) at longer wavelength (>400 nm). It is due to efficient p-acidity of the ligands. On comparing with Gold(III)

complexes of 1-alkyl-2-(ary-lazo)imidazoles, pyridyl-thioazophenolates and other pyridylthioether ligands the transitions at 430 nm is assigned to MLCT [d(Au) -- p* (naphthyl-azo-imidazole)] and, the band at 370 nm may be a mixture of (PPh_3)--Au(II)) and ligand centered p–p* transitions (Fig. 2).

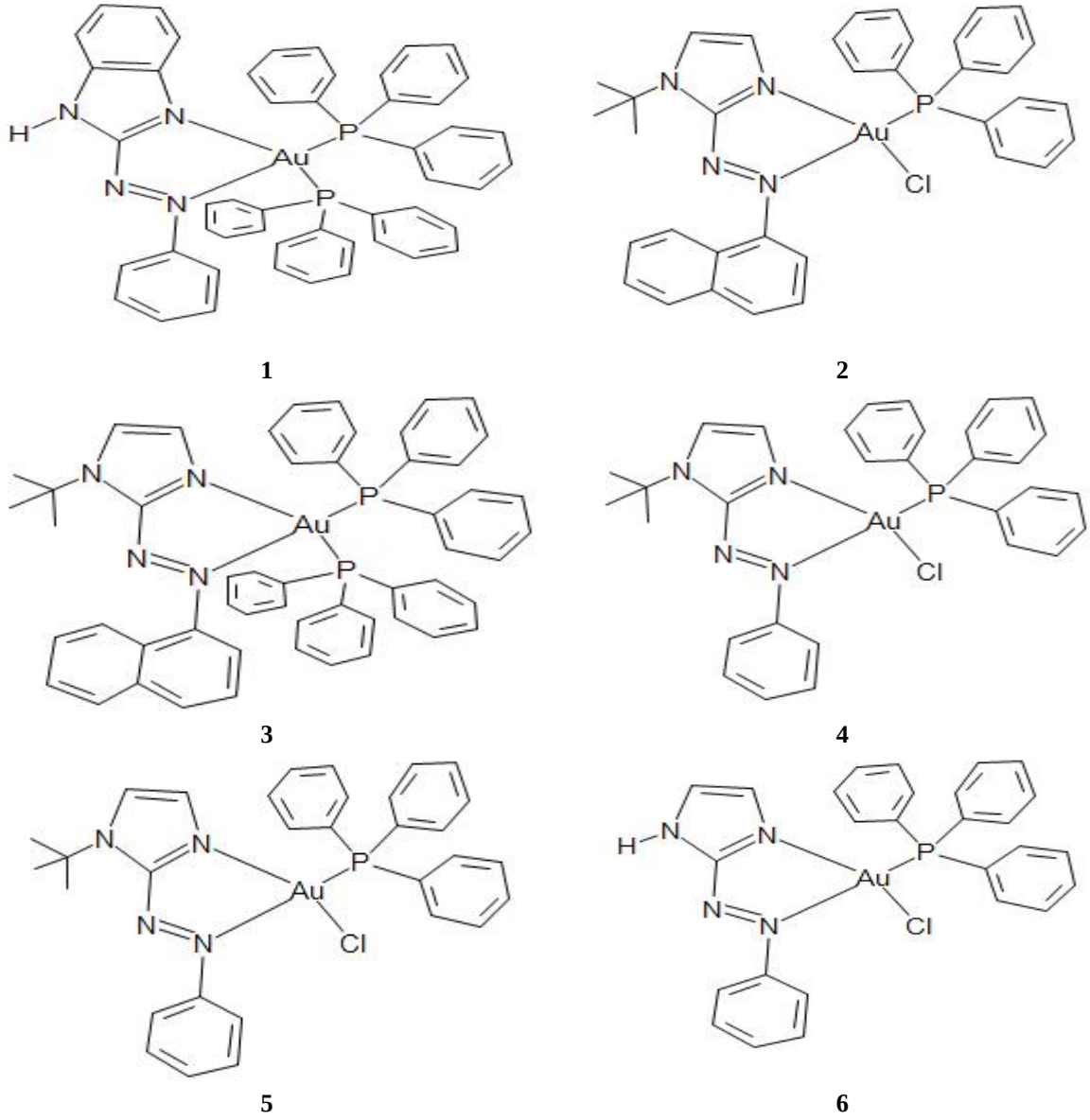

Fig. 1: Reaction scheme and all the complexes of Gold from complex 1 to complex 6, [$Au(PPh_3)_2(NaaiR^{/})$] and [$Au(PPh_3)(Cl)(NaaiR^{/})$], [$NaaiR^{/}$ = naphthyl-azo imidazole /benzimidazole /pyridine = $C_{10}H_4$-N=N- / C_3H_2-NN-1-$R^{/}$, (R imidazole) / C_7H_4-NN-1-H (Benzimidazole), / C_3H_4-N-(Pyridine), abbreviated as N,$N^{/}$-chelator, where N(imidazole) and N(azo) represent N and $N^{/}$, respectively; $R^{/}$ = H(*a*), Me (*b*), PPh_3 = Triphenyl phosphine, PPh_3]

The ^1H n.m.r. spectra, measured in CD_2Cl_2, of [$Au(PPh_3)_2(NaaiR^{/})$] and [$Au(PPh_3)(Cl)(NaaiR^{/})$], [$NaaiR^{/}$ = naphthyl-azo imidazole /benzimidazole /pyridine = $C_{10}H_4$-N=N- / C_3H_2-NN-1-$R^{/}$, (R imidazole) / C_7H_4-NN-1-H (Benzimidazole), / C_3H_4-N-(Pyridine), abbreviated as N,$N^{/}$-chelator, where N(imidazole) and N(azo) represent N and $N^{/}$, respectively; $R^{/}$ = H(*a*), Me (*b*), PPh_3 = Triphenyl phosphine, PPh_3]. were unambiguously assigned on comparing with [$Au(H_2O)$] and the free ligand ($NaaiR^{/}$). Imidazole 4- and 5-H appear as doublet at the lower frequency side of the spectra (7.0-7.6 ppm for 4-H; 6.4-7.0 ppm for 5-H). The aryl protons (7-H—11-H) of (*7-9)* are downfield shifted by 0.1-0.5 ppm as compared to those of the parent derivatives. They are affected by substitution; 8- and 10-H are

severely perturbed due to changes in the electronic properties of the substituents in the C(9)-position. The aryl protons 7-(7′-) and 11-(11′-)H resonate asymmetrically indicative of a magnetically anisotropic environment even in the solution phase.

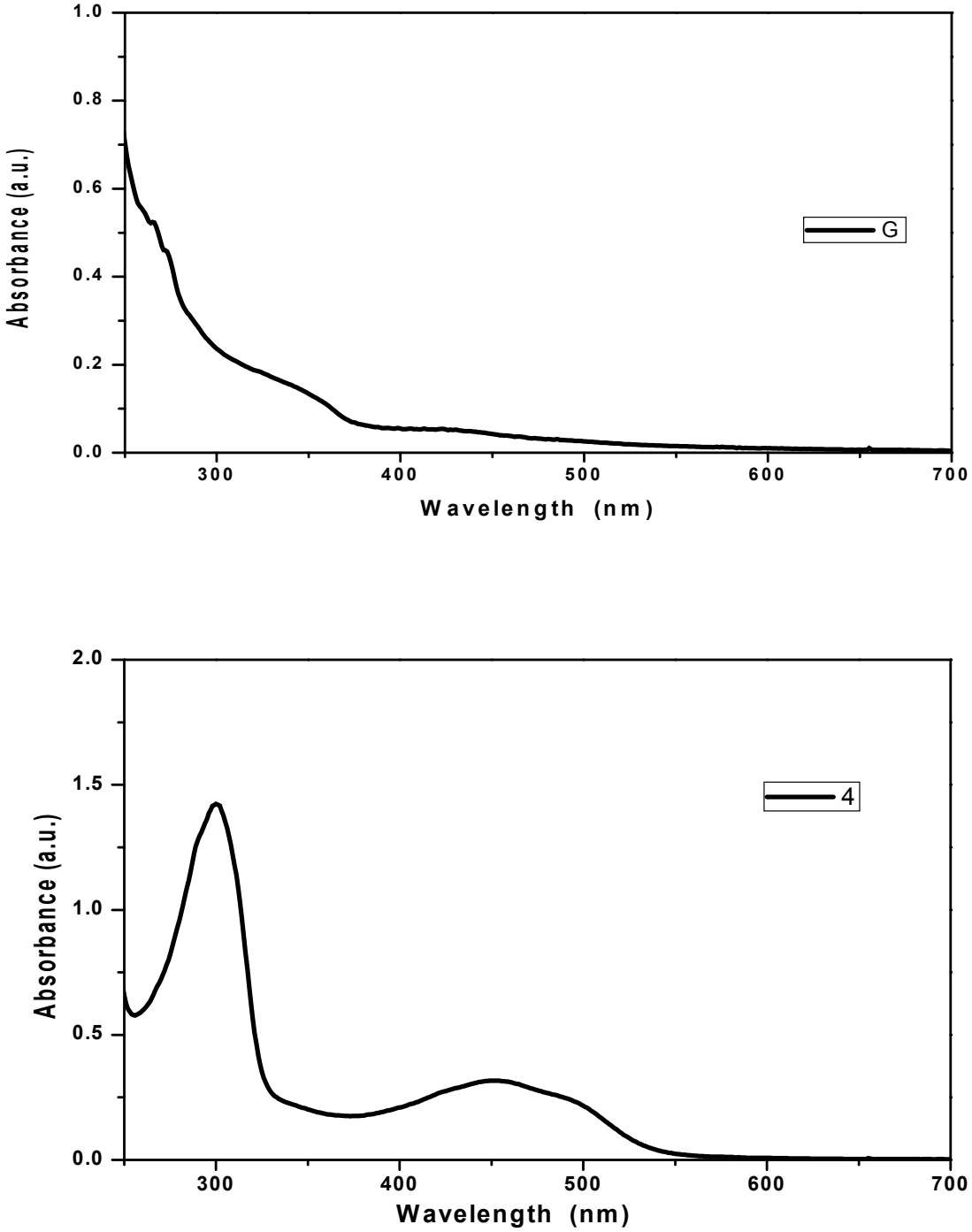

Figure 2: UV-Vis Spectroscopic data, (λ nm), of complex [Au(PPh$_3$)$_2$(NaaiR$^/$)] , complex 3 and [Au(PPh$_3$)(Cl)(NaaiR$^/$)], complex 2, [NaaiR$^/$ = naphthyl-azo imidazole /benzimidazole /pyridine = C$_{10}$H$_4$-N=N- / C$_3$H$_2$-NN-1-R$^/$, (R imidazole) / C$_7$H$_4$-NN-1-H (Benzimidazole), / C$_3$H$_4$-N-(Pyridine)] .

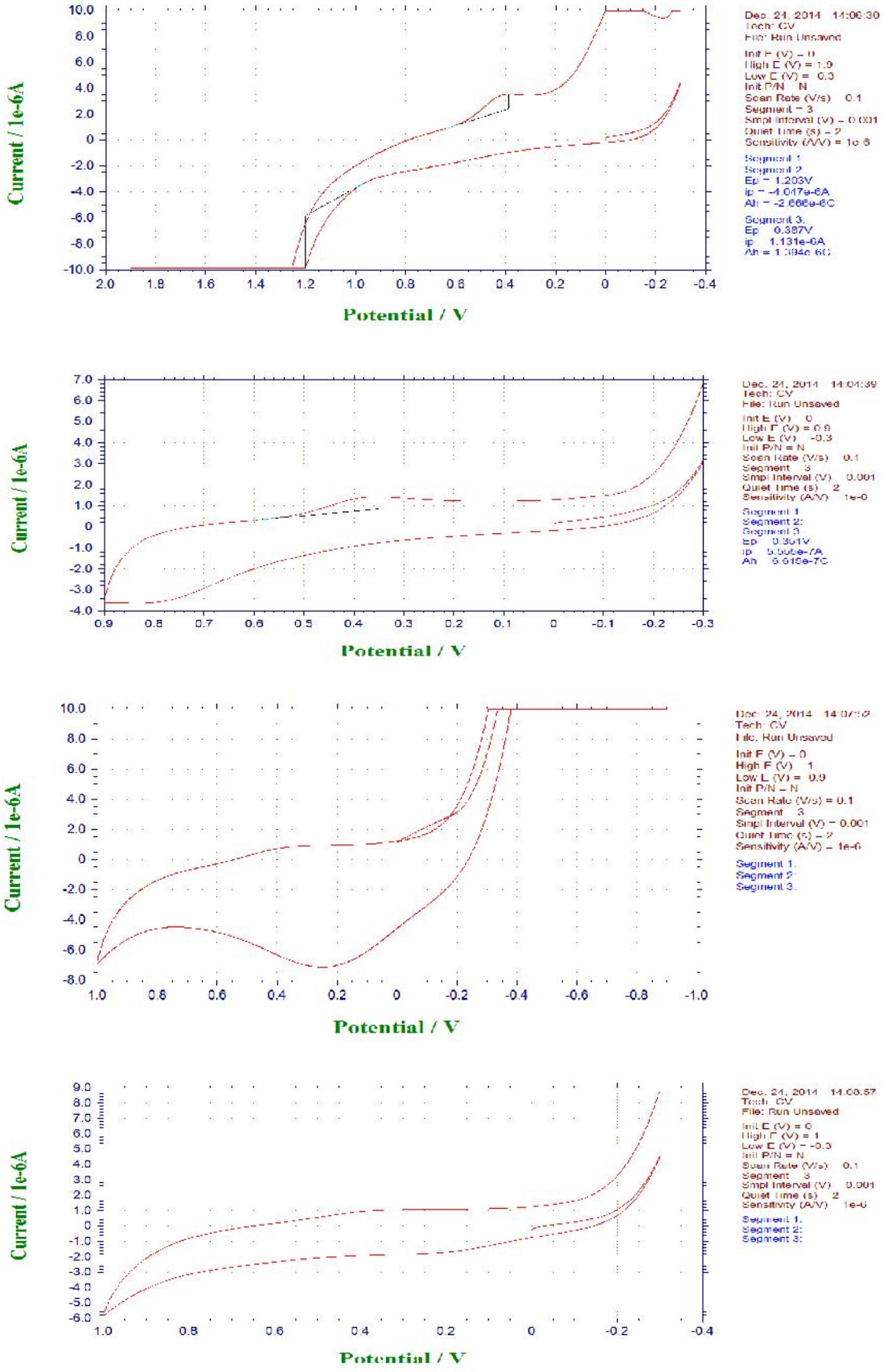

Figure 3: Electrochemistry or Cyclic Voltammetric data ($E_{1/2}$ (V) (E_p(mV) [Solvent MeCN, Supporting Electrolyte, Bu_4NClO_4 (0.1 M), scan rate 50 mVs^{-1}, Pt disk working electrode, Pt wire auxiliary electrode, referance electrode SCE at 298 K] of complex 1 (above two) and 2 (below two).

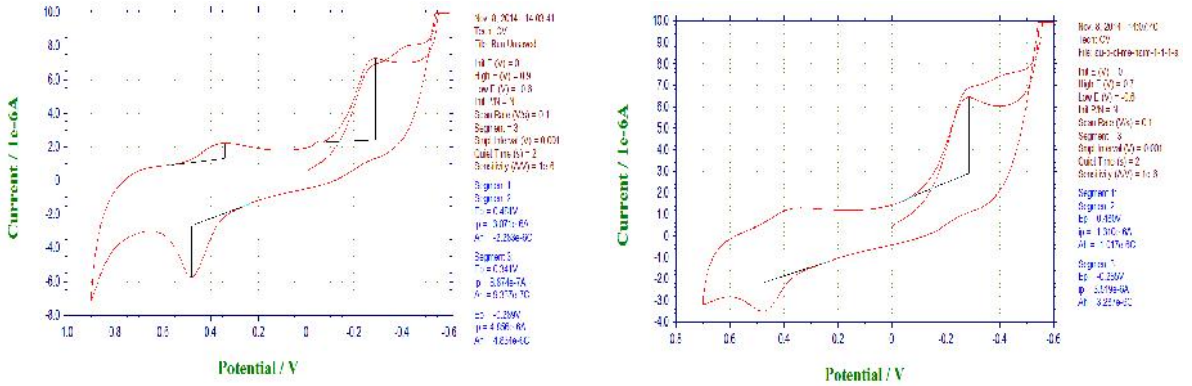

Figure 4: Electrochemistry or Cyclic Voltammetric data ($E_{1/2}$ (V) (E_p(mV) [Solvent MeCN, Supporting Electrolyte, Bu_4NClO_4 (0.1 M), scan rate 50 mVs^{-1}, Pt disk working electrode, Pt wire auxiliary electrode, referance electrode SCE at 298 K] of complex 3.

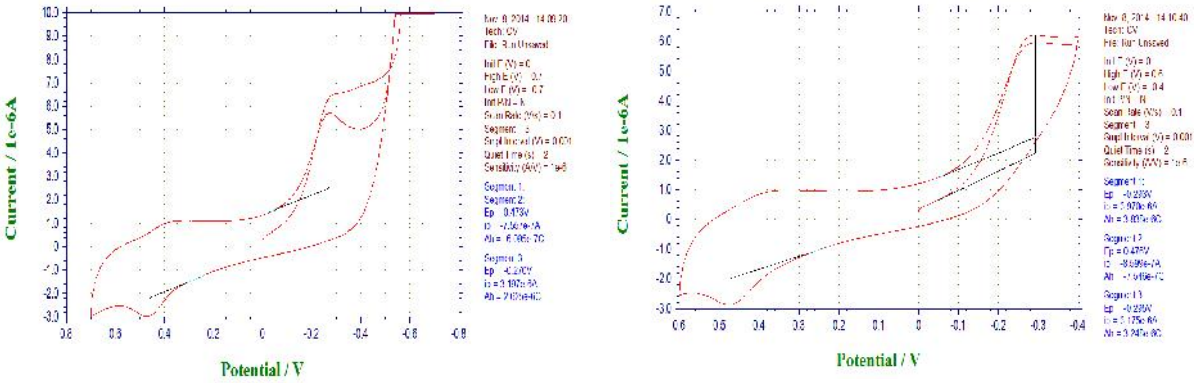

Figure 5: Electrochemistry or Cyclic Voltammetric data ($E_{1/2}$ (V) (E_p(mV) [Solvent MeCN, Supporting Electrolyte, Bu_4NClO_4 (0.1 M), scan rate 50 mVs^{-1}, Pt disk working electrode, Pt wire auxiliary electrode, referance electrode SCE at 298 K] of complex 2 .

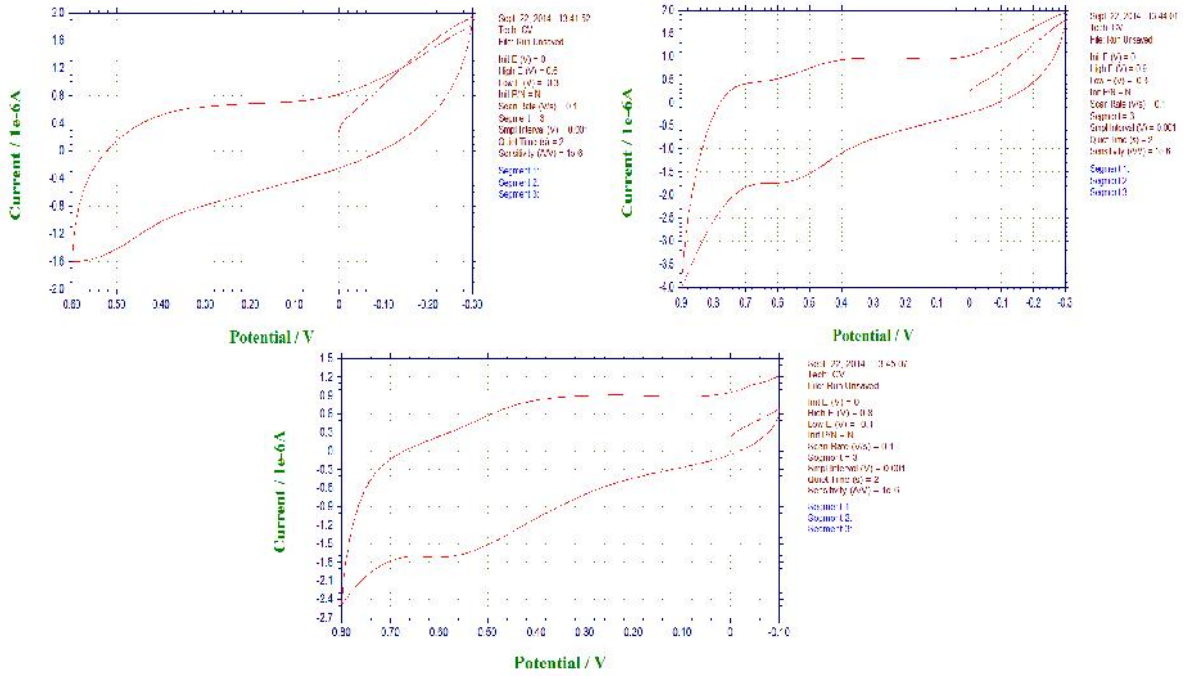

Figure 6: Electrochemistry or Cyclic Voltammetric data ($E_{1/2}$ (V) (E_p(mV) [Solvent MeCN, Supporting Electrolyte, Bu_4NClO_4 (0.1 M), scan rate 50 mVs^{-1}, Pt disk working electrode, Pt wire auxiliary electrode, referance electrode SCE at 298 K] of complex 4.

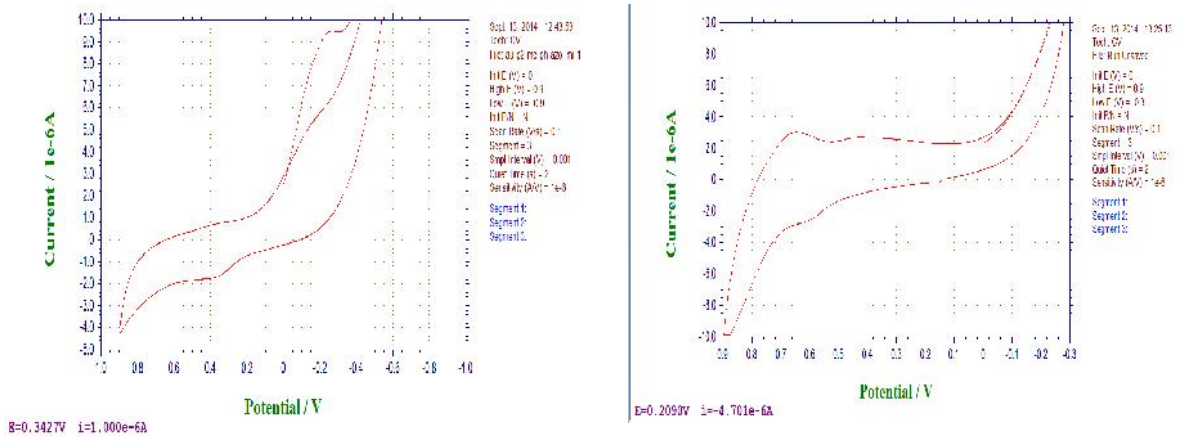

Figure 7: Electrochemistry or Cyclic Voltammetric data ($E_{1/2}$ (V) (E_p(mV) [Solvent MeCN, Supporting Electrolyte, Bu_4NClO_4 (0.1 M), scan rate 50 mVs^{-1}, Pt disk working electrode, Pt wire auxiliary electrode, referance electrode SCE at 298 K] of complex 5.

The ^{13}C NMR spectrum, measured in CD_2Cl_2, provides direct information about the carbon skeleton of the molecule $[Au(PPh_3)_2(NaaiR^{/})]$ and $[Au(PPh_3)(Cl)(NaaiR^{/})]$, [$NaaiR^{/}$ = naphthyl-azo imidazole /benzimidazole /pyridine = $C_{10}H_4$-N=N- / C_3H_2-NN-1-$R^{/}$, (R imidazole) / C_7H_4-NN-1-H (Benzimidazole), / C_3H_4-N-(Pyridine), abbreviated as N,$N^{/}$-chelator, where N(imidazole) and N(azo) represent N and $N^{/}$, respectively; $R^{/}$ = H(*a*), Me (*b*), PPh_3 = Triphenyl phosphine, PPh_3]. The carbon atom adjacent to the benzimidazole, naphthyl, molecule in the complex resonance at a lower field resulting of the conjugative effect of the phenyl ring with more electronegative pi-conjugate system. The non-protonated carbon atoms at C(2) and C(6) of the naphathylazoimidazole moiety is shifted farthest downfield in the spectrum.

Electrochemistry

Fig. 3, Fig. 4, Fig. 5, Fig. 6 and Fig. 7 shows representative cyclic voltammogram of the complexes and data are collected in Experimental Section. Gold(III) complexes, $[Au(PPh_3)_2(NaaiR^{/})]$ and $[Au(PPh_3)(Cl)(NaaiR^{/})]$, [$NaaiR^{/}$ = naphthyl-azo imidazole /benzimidazole /pyridine = $C_{10}H_4$-N=N- / C_3H_2-NN-1-$R^{/}$, (R imidazole) / C_7H_4-NN-1-H (Benzimidazole), / C_3H_4-N-(Pyridine), abbreviated as N,$N^{/}$-chelator, where N(imidazole) and N(azo) represent N and $N^{/}$, respectively; $R^{/}$ = H(*a*), Me (*b*), PPh_3 = Triphenyl phosphine, PPh_3], show a quasireversible oxidative response at 0.4 V which may be referred to Au(III)/Au(I). An irreversible response is observed at 1.0 V that may be assigned to the oxidation of water present in solvent. On scanning to ve direction up to 1.8 V we observe an irreversible response E pc at 0.4 V and a quasireversible response at 1.1 to 1.3 V. They may be assigned to reduction of azo group [(–N@N–)/(–N@N–)] of the chelated ligands. This observation suggests low heterogeneous electron-transfer rate constant which has been influenced by the applied potential. In general, the electrochemical reduction of Gold(III) complexes is associated with change in coordination geometry. Solution structure of Gold(III) complex shows square pyramidal or trigonal bipyramidal which upon reduction rearranges fast to tetrahedral geometry via bond rupture and bond formation. Two couples at ca.0.5 and 1.2 V are assigned to azo reduction. The quasi-reversibility of the couples is noted by peak-to-peak separation.

CONCLUSION

This work describes the isolation of a novel series of copper(II) azo-imine mononuclear and binuclear azide bridzed complexes, Gold(III) complexes, $[Au(PPh_3)_2(NaaiR^{/})]$ and $[Au(PPh_3)(Cl)(NaaiR^{/})]$, [$NaaiR^{/}$ = naphthyl-azo imidazole /benzimidazole /pyridine =

$C_{10}H_4$-N=N- / C_3H_2-NN-1-R$^{/}$, (R imidazole) / C_7H_4-NN-1-H (Benzimidazole), / C_3H_4-N- (Pyridine), abbreviated as N,N$^{/}$-chelator, where N(imidazole) and N(azo) represent N and N$^{/}$, respectively; R$^{/}$ = H(*a*), Me (*b*), PPh_3 = Triphenyl phosphine, PPh_3], and their spectral and elemental characterisation. The complexes were well characterised by NMR, IR, UV-VIS, CV, Mass spectroscopy. The voltammogram also shows a small anodic peak at 0.400 V.

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