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Gold (III)-2,2'-Bipyridine(bpy)-Arylazoimidazole (RaaiR') Complexes: Synthesis and Spectral Characterisation

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ABSTRACT

Reaction of $[\text{Au}(\text{bpy})\text{Cl}_2]\text{PF}_6$ with AgOTf followed by ligand addition leads to $[\text{Au}(\text{bpy})(\text{RaaiR}')]$ in low yield whereas direct substitution gives high yield. $[\text{RaaiR}' = p\text{-R-C}_6\text{H}_4\text{-N=N-C}_3\text{H}_2\text{-NN-1-R}'$, (I-3), abbreviated as $\text{N,N}'$ -chelator, where $\text{N}(\text{imidazole})$ and $\text{N}(\text{azo})$ represent N and N' , respectively; $\text{R} = \text{H}$ (a), Me (b), Cl (c) and $\text{R}' = \text{Me}$ (1), CH_2CH_3 (2), CH_2Ph (3), OSO_2CF_3 is the triflate anion, bpy is 2,2'-bipyridine]. The ^1H NMR spectral measurements suggest methylene, $-\text{CH}_2-$, in RaaiEt gives a complex AB type multiplet while in RaaiCH_2Ph it shows AB type quartets. ^{13}C NMR spectrum reflect molecular skeleton. In the $^1\text{H}-^1\text{H}$ COSY spectrum of the present complexes and contour peaks in the $^1\text{H}-^{13}\text{C}$ HMQC spectrum in the present complexes, assign the solution structure.

Keywords: gold (III), arylazoimidazole, NMR, IR, ESIMS, bpy.

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INTRODUCTION

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 (Alejandro Gutiérrez et al., 2013; Yukatsu Shichibu et al., 2013; Zhongping Ou et al., 2013; Sang Ho Lim et al., 2013; Mehm et al., 2013; Celik et al., 2013; Athanassios C. Tsipis et al., 2013; Camille Latouche et al., 2012). 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, glutathione, thiomalic acid, 2,3-dimercaptopropanol, and albumin has been studied. The reactivity of gold occurs through 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 arthritis 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. 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. The underlying "aurophilic" bonding has been analyzed in theoretical studies. The transfer of an organic group to a gold centre is traditionally carried out using organolithium compounds, Grignard reagents or organomercurials. There are however alternative transmetallation agents, which are particularly attractive because of their insensitivity to air and moisture, their mild reaction conditions and simple work-up. These include organotin compounds and boronic acids. Whilst the former have been used in the preparation of both gold compounds, the latter are so far limited to gold compounds represent interesting alternatives to other metal-based luminescent compounds with a d electron configuration. For Pd and Pt complexes (in the absence of metal-metal interactions) the emissive excited state is either a metal-to-ligand charge transfer (MLCT) or an intraligand (IL) transition (or a mixture of both) and of triplet-character (phosphorescence). Their metal centred transitions are usually at high energy and do not strongly influence the luminescence properties, which is important as these dd-states usually lead to a very efficient radiationless deactivation of the excited state (*Víctor Rojas-Cervellera, Ernest Giralt, and Carme Rovira, 2012; Dmitriy S. Dolzhenkov et al., 2012; Mao-Sheng Miao et al., 2012; Lei Gao et al., 2012; Laura Rodríguez et al., 2012; Volodymyr Smetana et al., 2012; Igor O. Koshevoy et al., 2012; Madanakrishna Katari et al., 2012; Atiya T. Overton et al., 2012; Yifeng Wang et al., 2012; Yu-Peng Zhou et al., 2012; Gemma E. Craig et al., 2012; Javier A. Cabeza et al., 2012; Ping Chai et al., 2012; Maria Serratrice et al., 2012*). Au(III) complexes are much less investigated due to some preconditions which have to be fulfilled for an emissive behaviour: because of the high oxidation potential of gold in the oxidation state +3 a MLCT is not favoured. For these complexes containing ligands with an extended π -system an emissive IL excited state is feasible, but the energetically low lying dd-states quench potential emissive states of most Au(III) complexes. However, these dd-states can be destabilized by strong field ligands diminishing the radiationless deactivation. Consequently, several cyclometallated complexes of the general formula $[\text{Au}(\text{C}-\text{N})\text{L}_2]^{n+}$ ($\text{C}-\text{N} = 2$ -phenylpyridine type ligand; L = acetylide, NHC; $n = 0$ or 2) and similar complexes bearing pincer type ligands including 2,6-diphenylpyridine or 6-phenyl-2,2'-bipyridine were reported to feature luminescence even in fluid solution at room temperature (*Hanan E. Abdou et al., 2012; Marco Baron et al., 2012; Bin Li, et al., 2012; Pedro I. da et al., 2012; Naweena Dahal et al., 2012; Tina H. T. Hsu et al., 2012; Kolle E. Thomas, et al., 2011; Zhongping Ou et al., 2011*). The emissions are mostly assignable to an IL-transition and sometimes these complexes also show a dual emission of both IL and 3IL character. Luminescent cyclometallated Au(III) complexes were reviewed in 2011 and since then, several new examples of this type were published. To the best of our knowledge, there is only one report on a luminescent Au(III) complex bearing a biphenyl moiety: $[\text{Au}(\text{Ppy})(\text{Bip})]$ (Ppy = 2-phenyl-pyridine; Bip = biphenyl). However, the second chromophore (Ppy) complicates the precise assignment of the transition. Indeed, according to TD-DFT calculations, both a ligand-to-ligand charge transfer (3LLCT) $[\pi(\text{Bip}) \rightarrow \pi^*(\text{Ppy})]$ and 3 IL $[\pi(\text{Bip}) \rightarrow \pi^*(\text{Bip})]$ contribute to the excited state. For this reason, the complexes presented below are particularly valuable, because they allow the investigation of the discrete chromophoric Au(III)-biphenyl moiety (*Yuan Yuan et al., 2011; Jeffrey W. Hudgens et al., 2011; Margot Wenzel, et al., 2011; Olga Crespo et al., 2011;*

Elisabete Oliveira et al., 2011; Elisabete Oliveira, et al., 2011; Rubén Chico, et al., 2011; Hsin-Lun Wu, et al., 2011; Ilaria Biondi, et al., 2011; Corinna Wetzel, et al., 2011; Saroj L. Samal et al., 2011; José M. López-de-Luzuriaga, et al., 2011; Jai Anand Garg, et al., 2011). In 1973, Chatt and co-workers performed transition-metal-catalyzed reactions in water. Since then, there has been a tremendous effort in the development of new water-soluble organotransition-metal complexes with the practical and environmental benefits in mind. This is principally accomplished through ligand design; thus, a variety of water-soluble ligand systems has been developed and explored. The most successful and noted of these systems have been phosphines with water-soluble substituents, such as sulfonated aryl groups, ammonium groups, and carboxylated aromatic groups. Further, there has been much success with some nonaromatic groups such as tris(hydroxymethyl)phosphine (P(CH₂OH)₃). Another nonionic aliphatic water-soluble phosphine is the tetrabasic 1,3,5-triaza-7-phosphaadamantane (PTA). Due to its utility as a water-soluble ligand and in efforts to explore the unique chemistry of this ligand, Darenberg's group has been active in the investigation of the different facets of PTA. Further, PTA has been investigated in many different areas such as photoluminescence of gold(I) phosphine complexes and intermolecular hydrogen-metal interactions, as well as its use as a precursor to other novel phosphine amine compounds and ligands. [(*Roberto Cao, et al., 2011; H. V. Rasika Dias, et al., 2011; Doris Y. Melgarejo, et al., 2011; Adriana Ilie, Ciprian I. Rat et al., 2011; Qisheng Lin and John D. Corbett et al., 2011; Manoja K. Samantaray, et al., 2011; Carrie A. Simpson, et al., 2010; Angela M. Kuchison, et al., 2010; Maria José Calhorda, et al., 2010; Hong-Jhin You, et al., 2010; Camino Bartolomé, et al., 2010; Sebastián A. Suárez, et al., 2010; Masashi Saitoh, et al., 2010*) Classical coordination chemistry began by using water both as solvent and as ligand for many compounds. As this discipline of chemistry advanced, new ligands, complexes, and reactions were discovered that required completely anhydrous reaction conditions as well as special apparatus and techniques so as to keep water *out* of reactions. Today, the tide has turned and water is experiencing a renaissance as a solvent in inorganic and organometallic chemistry. This change, motivated largely by the ever-increasing awareness of environmental concerns in the design of industrially important chemical processes has been the main driving force in the exploration of water-based reactions and water-soluble catalysts. However, the vast majority of homogeneous catalysts available today are either insoluble or unstable in water; as a result, one key challenge for the inorganic/organometallic chemistry community today is the design and development of compounds that are both soluble and stable in aqueous medium. Syntheses of hetero-*tris*-chelates, [Ru(bpy)_n(RaaiR')_{3-n}](ClO₄)₂ [bpy = 2,2'-bipyridine; n = 1, n = 2) containing labile reaction centres are reported from Sinha's laboratory. But the gold chemistry with multinuclear NMR spectroscopy of this ligand system is totally unexplored. In this paper, we examine the reaction of RaaiR' on gold(III) bis-chloro-bpy derivatives and the products are isolated, [Au(bpy)(RaaiR')]³⁺ [RaaiR' = *p*-R-C₆H₄-N=N-C₃H₂-NN-1-R', (*I-3*), abbreviated as N,N'-chelator, where N(imidazole) and N(azo) represent N and N', respectively; R = H (*a*), Me (*b*), Cl (*c*) and R' = Me (*1*), CH₂CH₃ (*2*), CH₂Ph (*3*), bpy is 2,2'-bipyridine, OSO₂CF₃ is the triflate anion, tht is tetrahydrothiophen]. The complexes are well characterized by i.r., ¹H n.m.r., ¹³C n.m.r., ¹H-¹H COSY n.m.r., ¹H-¹³C HMQC and mass spectrometry.

EXPERIMENTAL

Material and Instrumentation

Published methods were used to prepare RaaiR' [5-7], [Au^{III}(bpy)(Cl)₂]⁺ [8-11]. All other chemicals and organic solvents used for preparative work were of reagent grade (SRL, Sigma Alhrich). The purification of MeCN used as solvent and other solvents were done following the literature method. 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 ^1H 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 $\sim 10^{-3}$ 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

[(2,2'-bipyridine){1-ethyl-2-(p-tolylazo)imidazole}aurate(III)]triflate, $[\text{Au}^{\text{III}}(\text{bpy})(\text{HaaiEt})](\text{OTf})_2(\text{PF}_6)_2$, **2b**

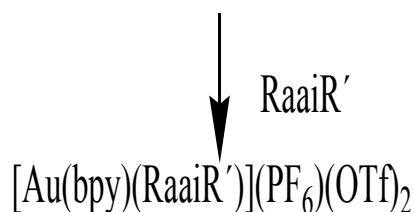
In path I, to a CH_2Cl_2 solution (15 cm^3) of $[\text{Au}^{\text{III}}(\text{bpy})\text{Cl}_2]$ (0.665 g, 0.10 mmol) $[\text{Ag}(\text{tht})(\text{OTf})]$ was added (1:2) and into this, was added yellow CH_2Cl_2 solution of 1-ethyl-2-(p-tolylazo)imidazole (0.020g, 0.10mmol), slowly, dropwise, and the mixture was stirred at 343-353 K for 2 h..

In path II direct ligand was added with the dichloro gold parent complexes following the stoichiometric ratio and the resulting solution was under stirring for 30 hr(product was isolated in a very high yield). Where respectively added the other ligands, HeaaiMe (0.0186 g, 0.1 mmol, 1a), MeaaiMe (0.020 g, 0.1 mmol, 1b), ClaiiMe (0.0220 g, 0.1 mmol, 1c), MeaaiEt (0.0214 g, 0.1 mmol, 2b), ClaiiEt (0.0235 g, 0.1 mmol, 2c), HaaiBz (0.0262 g, 0.1 mmol, 3a), MeaaiBz (0.0276 g, 0.1 mmol, 3b), ClaiiBz (0.0297 g, 0.1 mmol, 3c). The orange solution that resulted was concentrated (4 cm^3) and kept in a refrigerator overnight (1 h). The addition of hexane to the above red solution gives precipitate which was collected by filtration, washed thoroughly with hexane to remove excess ligand and then dried *in vacuo* over pump overnight. The yield was 0.088 g (80%). All other complexes were prepared similarly as stated above. Analysis for $[\text{Au}^{\text{III}}(\text{bpy})(\text{HaaiMe})]\text{PF}_6(\text{Cl})_2$, $[\text{C}_{20}\text{H}_{18}\text{N}_6\text{Au}]\text{PF}_6(\text{Cl})_2$, (1a), Calcd(found): C, 31.8(31.9), H, 2.4(2.6), N, 11.1(11.2); IR $\nu(\text{N}=\text{N})$ 1370 $\nu(\text{C}=\text{N})$ 1590 $\nu(\text{bpy})$ 1600,1150,1290; ESIMS, 755 $[\text{M}^+]$, 539 $[\text{M}-2\text{Cl},\text{PF}_6]$, Analysis for $[\text{Au}^{\text{III}}(\text{bpy})(\text{MeaaiMe})]\text{PF}_6(\text{Cl})_2$, $[\text{C}_{21}\text{H}_{20}\text{N}_6\text{Au}]\text{PF}_6(\text{Cl})_2$, (1b), Calcd(found): C, 32.8(32.9), H, 2.6(2.6), N, 10.9(10.8); IR $\nu(\text{N}=\text{N})$ 1379 $\nu(\text{C}=\text{N})$ 1599 $\nu(\text{bpy})$ 1610,1150,1299; ESIMS, 769 $[\text{M}^+]$, 553 $[\text{M}-2\text{Cl},\text{PF}_6]$, Analysis for $[\text{Au}^{\text{III}}(\text{bpy})(\text{ClaiiMe})]\text{PF}_6(\text{Cl})_2$, $[\text{C}_{19}\text{H}_{17}\text{N}_6\text{Au}]\text{PF}_6(\text{Cl})_2$, (1c), Calcd(found): C, 30.8(30.4), H, 2.1(2.2), N, 10.6(10.7); IR $\nu(\text{N}=\text{N})$ 1370 $\nu(\text{C}=\text{N})$ 1599 $\nu(\text{bpy})$ 1610,1150,1290; ESIMS, 789.5 $[\text{M}^+]$, 573.5 $[\text{M}-2\text{Cl},\text{PF}_6]$, Analysis for $[\text{Au}^{\text{III}}(\text{bpy})(\text{HaaiEt})]\text{PF}_6(\text{Cl})_2$, $[\text{C}_{21}\text{H}_{20}\text{N}_6\text{Au}]\text{PF}_6(\text{Cl})_2$, (2a), Calcd(found): C, 32.8(32.9), H, 2.4(2.6), N, 10.9(10.8); IR $\nu(\text{N}=\text{N})$ 1379 $\nu(\text{C}=\text{N})$ 1599 $\nu(\text{bpy})$ 1620,1150,1295; ESIMS, 769 $[\text{M}^+]$, 553 $[\text{M}-2\text{Cl},\text{PF}_6]$, Analysis for $[\text{Au}^{\text{III}}(\text{bpy})(\text{MeaaiEt})]\text{PF}_6(\text{Cl})_2$, $[\text{C}_{22}\text{H}_{22}\text{N}_6\text{Au}]\text{PF}_6(\text{Cl})_2$, (2b), Calcd(found): C, 33.8(33.7), H, 2.8(2.9), N, 10.7(10.8); IR $\nu(\text{N}=\text{N})$ 1370 $\nu(\text{C}=\text{N})$ 1590 $\nu(\text{bpy})$ 1600,1150,1290; ESIMS, 783 $[\text{M}^+]$, 567 $[\text{M}-2\text{Cl},\text{PF}_6]$, Analysis for $[\text{Au}^{\text{III}}(\text{bpy})(\text{ClaiiEt})]\text{PF}_6(\text{Cl})_2$, $[\text{C}_{21}\text{H}_{19}\text{N}_6\text{Au}]\text{PF}_6(\text{Cl})_2$, (2c), Calcd(found): C, 31.3(31.3), H, 2.4(2.6), N, 10.6(10.5); IR $\nu(\text{N}=\text{N})$ 1370 $\nu(\text{C}=\text{N})$ 1596 $\nu(\text{bpy})$ 1610,1150,1296; ESIMS, 803.5 $[\text{M}^+]$, 587.5 $[\text{M}-2\text{Cl},\text{PF}_6]$, Analysis for $[\text{Au}^{\text{III}}(\text{bpy})(\text{HaaiBz})]\text{PF}_6(\text{Cl})_2$, $[\text{C}_{26}\text{H}_{22}\text{N}_6\text{Au}]\text{PF}_6(\text{Cl})_2$, (3a), Calcd(found): C, 37.5(37.6), H, 2.7(2.6), N, 10.1(10.2); IR $\nu(\text{N}=\text{N})$ 1379 $\nu(\text{C}=\text{N})$ 1590 $\nu(\text{bpy})$ 1600,1155,1295; ESIMS, 831 $[\text{M}^+]$, 615 $[\text{M}-2\text{Cl},\text{PF}_6]$, Analysis for $[\text{Au}^{\text{III}}(\text{bpy})(\text{MeaaiBz})]\text{PF}_6(\text{Cl})_2$, $[\text{C}_{27}\text{H}_{24}\text{N}_6\text{Au}]\text{PF}_6(\text{Cl})_2$, (3b), Calcd(found): C, 38.4(38.3), H, 2.8(2.9), N, 9.9(9.9); IR $\nu(\text{N}=\text{N})$ 1375 $\nu(\text{C}=\text{N})$ 1595 $\nu(\text{bpy})$ 1600,1150,1290; ESIMS, 845 $[\text{M}^+]$, 629 $[\text{M}-2\text{Cl},\text{PF}_6]$, Analysis for $[\text{Au}^{\text{III}}(\text{bpy})(\text{ClaiiBz})]\text{PF}_6(\text{Cl})_2$, $[\text{C}_{26}\text{H}_{21}\text{N}_6\text{Au}]\text{PF}_6(\text{Cl})_2$, (3c), Calcd(found): C, 36.0(36.1), H, 2.4(2.6), N, 9.7(9.8); IR $\nu(\text{N}=\text{N})$ 1375 $\nu(\text{C}=\text{N})$ 1590 $\nu(\text{bpy})$ 1600,1150,1290; ESIMS, 865.5 $[\text{M}^+]$, 649.5 $[\text{M}-2\text{Cl},\text{PF}_6]$.

RESULTS AND DISCUSSION

Synthesis and Formulation

Path I



40% yield

Path II

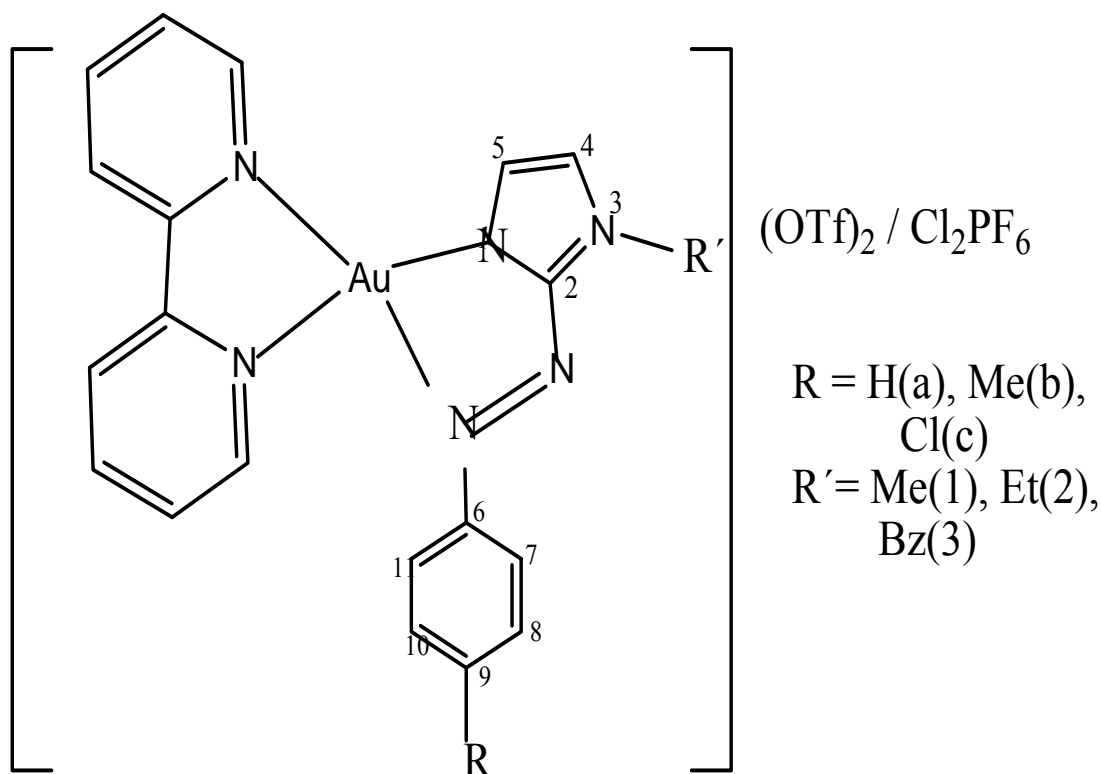
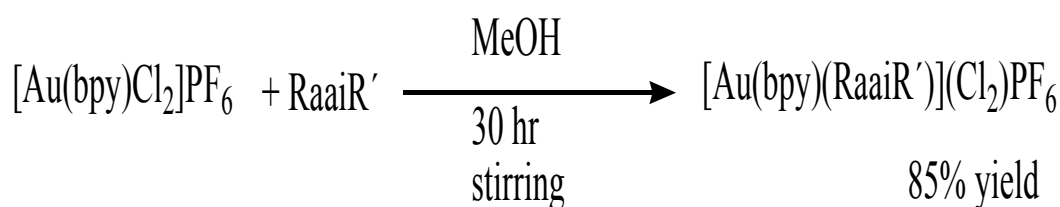


Figure 1: Synthesis of the complexes in two different paths and formulation of the product

The complexes, $[\text{Au}^{\text{III}}(\text{bpy})(\text{RaaiR}')^3]^3+$ [$\text{RaaiR}' = p\text{-R-C}_6\text{H}_4\text{-N=N-C}_3\text{H}_2\text{-NN-1-R}'$, (1-3), abbreviated as N,N'-chelator, where N(imidazole) and N'(azo) represent N and N', respectively; R = H (a), Me (b), Cl (c) and R' = Me (1), CH₂CH₃ (2), CH₂Ph (3), bpy=2,2'-bipyridine, OSO₂CF₃ is the triflate anion, tht is tetrahydrothiophen], were prepared by removing tht from $[\text{Au}^{\text{III}}(\text{bpy})(\text{tht})_2]^3+$, with RaaiR' under stirring at 343-353 K in dichloromethane solution in good yield (75-80%). In path II direct ligand was added

following the stoichiometric ratio and the resulting solution was under stirring for 30 hr (high yield). The synthetic routes are shown in *Scheme 1*. The composition of the complexes is supported by microanalytical results. The red orange complexes are soluble in common organic solvents but insoluble in H₂O, methanol, ethanol. In MeCN, the complexes, (*I-3*) behave as 1:3 electrolytes ($\Lambda_M = 90\text{-}120 \Omega^{-1}\text{cm}^{-1}\text{mol}^{-1}$).

Spectral Studies

I.r. spectra of the complexes, $[\text{Au}^{\text{III}}(\text{bpy})(\text{RaaiR}')^3]^+$ show a 1:1 correspondence to the spectra of the bromo analogue, except the appearance of intense stretching at 1365-1370 and 1570-1580 cm^{-1} with concomitant loss of $\nu(\text{Au-Cl})$ at 320-340 cm^{-1} . They are assigned to $\nu(\text{N=N})$ and $\nu(\text{C=N})$ appear at 1365-1380 and 1570-1600 cm^{-1} , respectively. Other important frequencies are $\nu(\text{bpy})$ at 1110-1120, 1200-1210, 1250-1260, 750-760, 695-700 and 500-510 cm^{-1} along with weak bands at 545-550 cm^{-1} .

The ESI mass spectrum of a MeCN 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.

Fluorine n.m.r., $^{19}\text{F}\{\text{H}\}$, of the present series of complexes show a sharp peak at -78 for the presence of triflate ion.

The ^1H n.m.r. spectra of $[\text{Au}^{\text{III}}(\text{bpy})(\text{RaaiR}')](\text{OTf})_2$ (*I-3*) complexes were unambiguously assigned (Figure 1,2) on comparing with parent complexes and the free ligand (RaaiR'). Complexes may exist in two different geometric isomers and with reference to coordination pairs of N(imidazole), N and N(azo), N' they are *trans-cis* (*tc*), *cis-trans* (*ct*) (Isomer A,B). The solution ^1H NMR spectra support at least the presence of two isomers in different proportion.

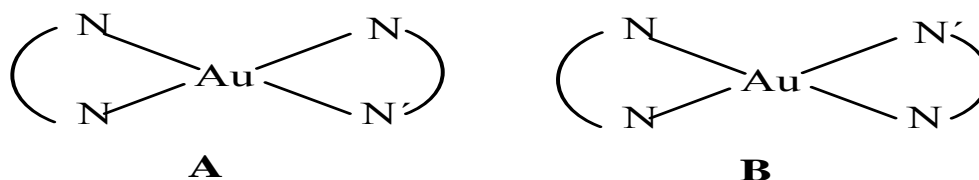


Figure 2: Different Isomer A and B of the complexes

The aryl protons (7-H-11-H) of (7-9) are downfield shifted by 0.1-0.7 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. Imidazole 4- and 5-H appear as doublet at the lower frequency side of the spectra (7.0-7.2 ppm for 4-H; 6.9-7.1 ppm for 5-H). The proton movement upon substitution (9-R) is corroborated with the electromeric effect of R. The aryl protons 7-(7'-) and 11-(11'-)H resonate asymmetrically indicative of a magnetically anisotropic environment even in the solution phase. The 1-R' [R' = Me, CH₂CH₃, CH₂(Ph)] exhibit usual spin-spin interaction. 1-Me appears as a singlet at 2.0 ppm for $[\text{Au}(\text{bpy})(\text{RaaiMe})]^3+$; the methylene protons, 1-CH₂-(CH₃) show AB type quartet (ca. 4.4, 4.6 ppm) and (1-CH₂)CH₃ gives a triplet at 1.5 ppm (7.0-8.0 Hz) for $[\text{Au}(\text{bpy})(\text{RaaiCH}_2\text{CH}_3)]^3+$. 1-CH₂(Ph) protons appear at AB type quartets (ca. 5.5, 5.7 ppm) with geminal coupling constant avg. 8.8 Hz in $[\text{Au}(\text{bpy})(\text{RaaiCH}_2\text{Ph})]^3+$ (Fig. 3 and Fig. 4, Table 1).

The ^{13}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 on nine complexes and the data are given on experimental section (Fig. 1,2). 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-CC=CC-.

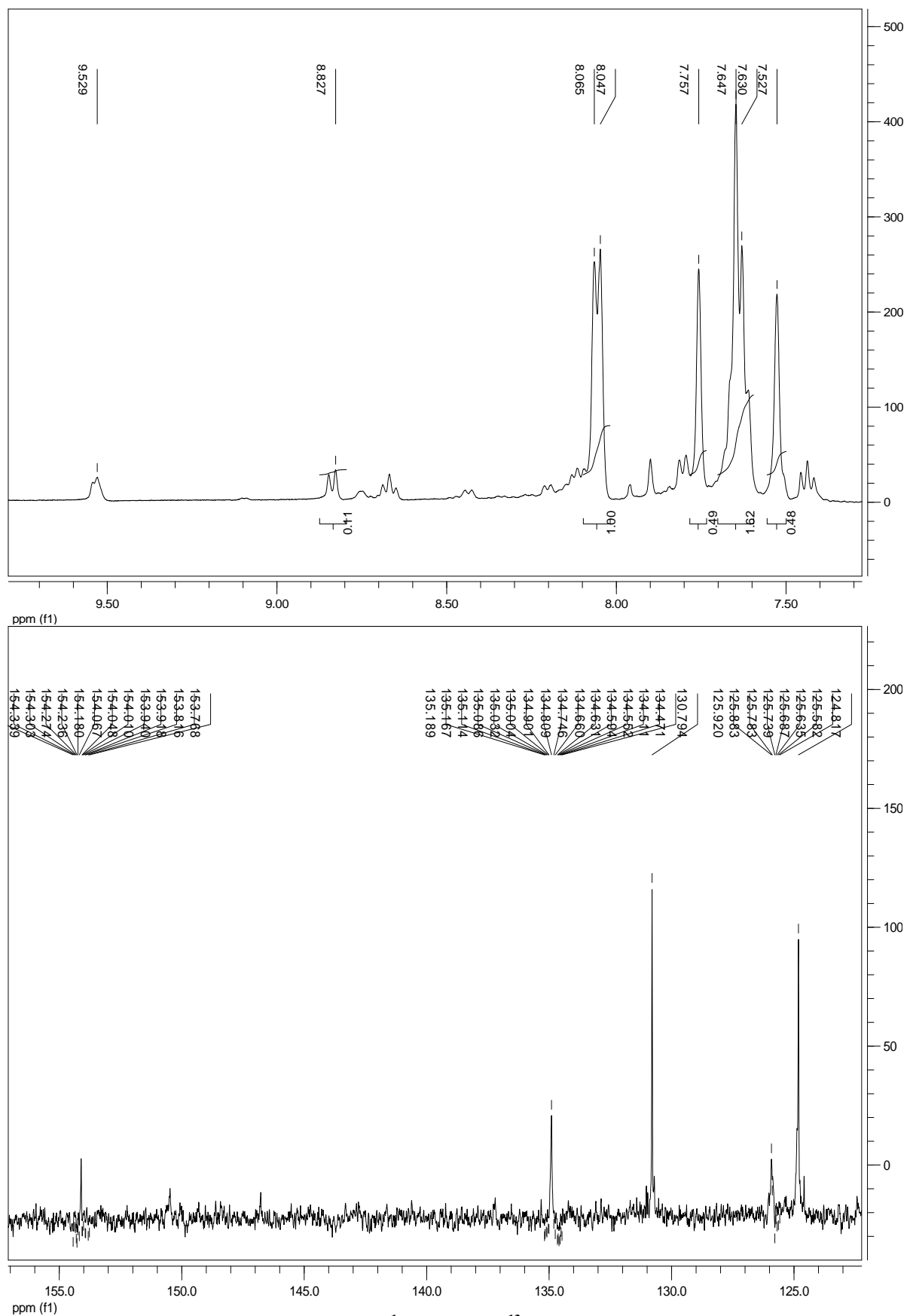


Figure 3: Aromatic region ¹H NMR and ¹³C (H) NMR of complex (2a)

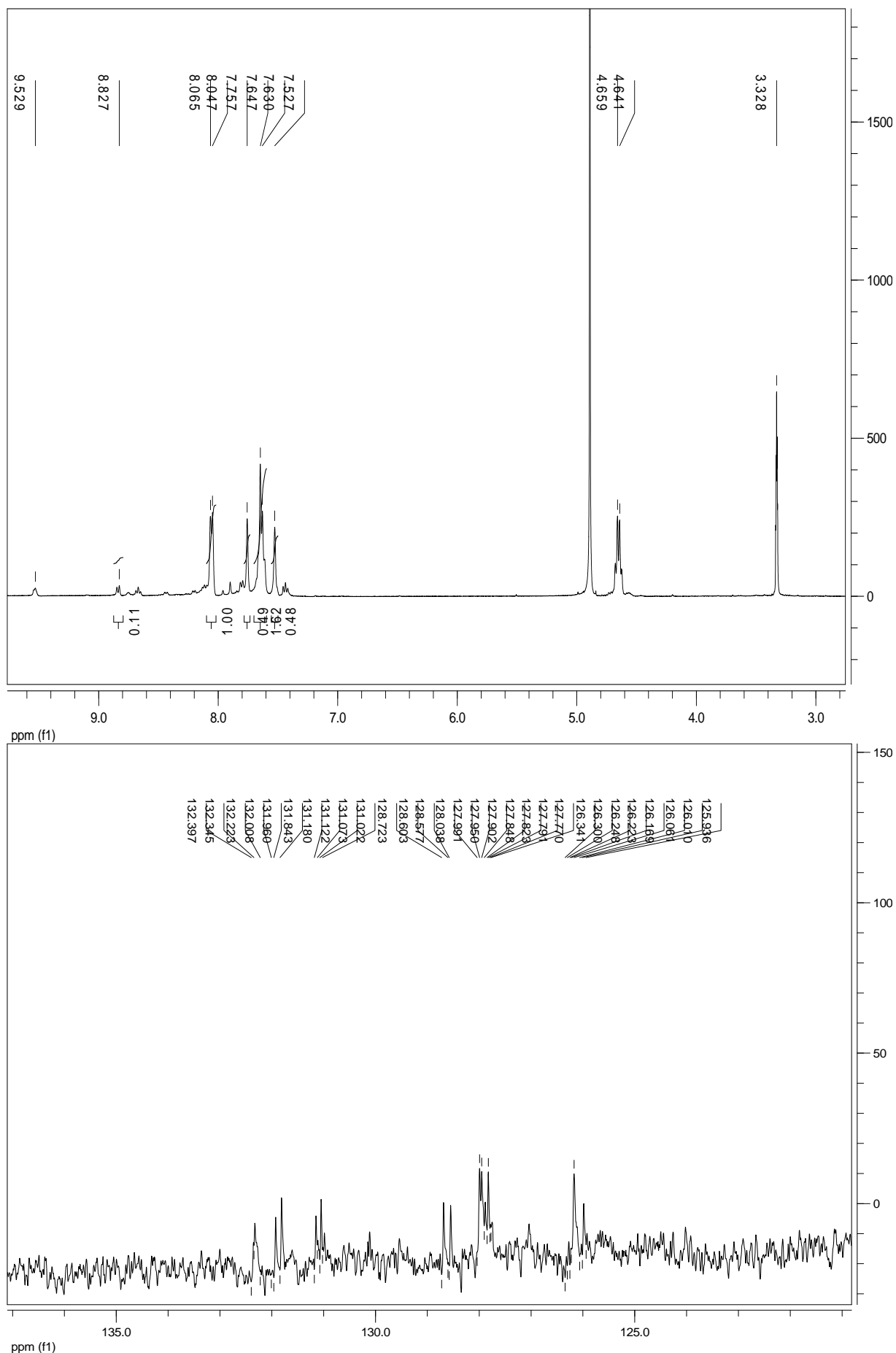


Figure 4: Complete ^1H NMR and ^{13}C (H) NMR of complex (2b)

Table 1: ¹H-n.m.r. spectral data, δ (J/Hz), ppm in CDCl₃ and cyclic voltammetric data^g of the complexes

Compd.	a,a'-H	b,b'	c,c'	4-H ^c	5-H ^c	7,11-H ^c	8,10-H	N-CH ₃	N-CH ₂	d,d'	-E ^{L1} -E ^{L2} -E ^{L3}		
											Units in V (ΔE_p in mV)		
(1a) ^a	9.5(5)	8.8(7)	8.6(4)	7.55(7.5)	7.46 (7.5)	8.03 (8.1)	7.75 (8.1) ^d	4.09 ^f	-	8.4(9)	0.33 0.69 0.9	(75) (110)	
(1b)	9.6(7)	8.8(7)	8.7(8)	7.58 (7.5)	6.96 (7.5)	8.07 (8.1)	7.84 (8.1) ^c	4.17 ^f	-	8.3(3)	0.39 0.68 0.98	(90) (120)	
(1c)	9.5(5)	8.8(7)	8.6(4)	7.3 (8.1)	7.42 (8.1)	8.05 (7.8)	7.85 (7.8) ^c	4.16 ^f	-	8.4(5)	0.30 0.67 0.97	(80) (110)	
(2a) ^a	9.2(5)	8.9(8)	8.6(9)	7.4 (7.5)	7.00 (7.5)	8.01 (7.8)	7.75 (8.1) ^d	1.52(8.1) ^d	4.62,4.65 (10.0) ^e	8.1(9)	0.30 0.65 0.96	(75) (120)	
(2b)	9.5(5)	8.8(7)	8.6(4)	7.53 (8.1)	7.24 (8.1)	8.01 (7.5)	7.72 (7.5) ^c	1.58(8.1) ^d	4.64,4.56 (10.0) ^e	8.4(3)	0.40 0.70 0.95	(80) (110)	
(2c)	9.5(5)	8.4(3)	8.1(5)	7.34 (8.1)	7.36 (8.1)	8.04 (7.5)	7.76 (7.5) ^c	1.55(8.1) ^d	4.64,4.53 (11.0) ^e	8.1(9)	0.29 0.61 0.94	(90) (110)	
(3a) ^a	9.5(5)	8.8(7)	8.6(4)	7.56 (7.8)	7.48 (7.8)	8.08 (8.1)	7.78 (8.1) ^d	-	5.68,5.73 (15.0) ^g	8.4(9)	0.28 0.60 0.93	(70) (120)	
(3b)	9.5(5)	8.1(7)	8.1(6)	7.47 (8.1)	6.99 (8.1)	8.01 (8.1)	7.70 (8.1) ^c	-	5.46,5.73 (17.0) ^g	8.2(9)	0.36 0.70 0.94	(70) (120)	
(3c)	9.5(5)	8.8(7)	8.6(4)	7.11 (7.8)	7.32 (7.8)	8.15 (8.1)	7.78 (8.1) ^c	-	5.44,5.70 (18.0) ^g	8.4(3)	0.28 0.62 0.96	(90) (100)	

^a δ (9-H) 7.45 ppm(m); ^b δ (9-Me); ^c doublet; ^d triplet; ^e AB type sextet, geminal coupling constant; ^f 1-Me, singlet; ^g AB type quartet, geminal coupling constant; ^h Phenyl-H; ⁱ Solvent, MeCN, supporting electrolyte : nBu₄NClO₄ (0.1M), working electrode : GC milli electrode, auxiliary electrode : Pt – wire, reference electrode : SCE, solute concentration : $\sim 10^{-3}$ M, scan rate : 50 mV s⁻¹, $\Delta E_p = | E_{pa} - E_{pc} |$ where E_{pa} = anodic peak potential and E_{pc} = cathodic peak potential ;

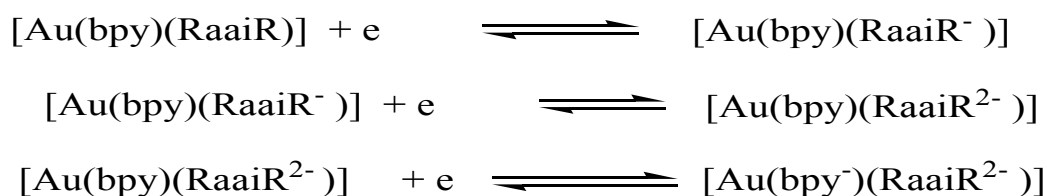
Table 2: ¹³C-NMR spectral data of [Au(bpy)(RaaiR')] in CDCl₃

Compd	2-C	6-C	4-C	5-C	7,11-C	8,10.-C	9-C	12-C	a,a'-C	b,b'-C	c,c'-C	d,d' C	N-Me,Et,Bz
(1a)	136.87	139.89	125.21	124.76	130.98	128.98	127.56	148.87	154.98	145.66	144.99	150	30.98
(1b)	136.87	139.89	125.21	124.76	131.98	127.98	126.56	149.87	152.98	145.66	144.99	154	31.98
(1c)	135.87	139.89	125.21	122.76	130.98	128.98	127.56	148.87	154.98	145.66	144.99	150	30.08
(2a)	135.87	139.89	125.21	123.76	131.98	127.98	127.56	147.87	154.98	144.66	144.99	151	30.98, 41.12
(2b)	135.87	139.89	125.21	124.76	130.98	128.98	127.56	148.87	150.98	145.66	144.99	153	31.98,42.09
(2c)	135.87	139.89	125.21	122.76	131.98	128.98	126.56	148.87	154.98	145.66	144.99	151	30.98,42.65
(3a)	135.87	139.89	124.21	124.76	130.98	128.98	127.56	148.87	154.98	145.66	144.99	152	31.98,128-132
(3b)	135.87	138.89	125.21	124.76	131.98	128.98	125.56	148.87	154.98	145.66	145.99	152	30.98,128-137
(3c)	135.87	139.89	125.21	124.76	130.98	128.98	127.56	148.87	150.98	145.66	144.99	153	30.98,129-138

Similarly the carbon atom adjacent to the PPh₃ 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 methyl carbon atom of the imidazole ring resonate at 30 ppm, reasonably compare to the other carbon atoms resonance(Fig. 3 and Fig. 4, Table 2).

In the COSY spectrum, absence of any off-diagonal peaks extending from $\delta = 14.1$ ppm and 9.5 ppm confirm their assignment of no proton on N(1) and N(3) respectively. However, extending horizontal and vertical lines from $\delta = 8.3$ ppm [C(8)H] and 8.6 ppm [C(10)H] encounter cross peaks at $\delta = 7.1$ ppm and 7.2 ppm, where the C(7)H and C(11)H resonances are merged into multiplets along with the phenyl ring proton resonances. The comparatively weaker coupling interactions of C(8)H and C(10)H 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 $\delta = 7.3$ ppm and 7.31 ppm. The ¹H-¹³C heteronuclear multiple-quantum coherence (HMQC) spectrum provides information regarding the interaction between the protons and the carbon atoms to which they are directly attached. Here, the absence of any contours at higher frequency region assign them C2, C6, C-*ipso*, carbon atoms respectively. This is because, they belong to the non-protonated carbon atoms on the imidazole, phenyl and aryl rings. So they are unable to show any direct ¹H-¹³C heteronuclear multiple-quantum coherence. The peaks observed at $\delta = 134, 131, 135$ ppm and 137 ppm assign them to the C(9), C(8), C(7), C(11), and C(10) carbon atoms respectively, due to their interaction with H resonance at $\delta = 7.4, 7.5, 7.8, 7.80$ ppm and 7.3 ppm.

The voltammogram show the ligand reductions at the negative to SCE. The electrochemical properties were examined cyclic voltammetrically at a glassy carbon working electrode in MeCN. In the potential range +2.0 to -2.0 V at the scan rate 50 mV s⁻¹ two redox couples are observed prominent and all are at the negative side of the voltammogram. First one is quasireversible as is evident from peak-to-peak separation value, $\Delta E_p > 110$ mV. The gold oxidation part is very negligible. One electron nature of the redox process is supported by the i_{pa}/i_{pc} ratio (i_{pa} = anodic peak current and i_{pc} = cathodic peak current) which varies -0.30 to -0.39 and -0.60 to -0.75 and -0.99-1.01(irrev). The azo group in RaaiR' may accommodate two electrons and hence two coordinated ligands should exhibit four reductive responses. However, within the available potential window two reductions were clearly observable as shown below. Third one is for the bipyridine molecule as expected from previous result of Ru-tris chelate complexes.



CONCLUSION

This work describes the isolation of a novel series of Gold(III) azo-imine complexes, $[\text{Au}^{\text{III}}(\text{bpy})(\text{RaaiR}')]^{3+}$ and their spectral and elemental characterisation. ¹H NMR study suggests quartet splitting of ethyl substitution. ¹³C (¹H)NMR study suggests molecular skeleton. ¹H-¹H COSY spectrum as well as contour peaks in the ¹H-¹³C HMQC spectrum

assign them to the carbon hydrogen atoms interaction. Electrochemistry assigns ligand reduction part rather than metal oxidation.

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