Full Length Research Paper

Organometallic gold (III) bis-pentafluorophenyl-arylazo imidazole: Synthesis and multinuclear NMR investigation

P. Byabartta

Departmento de Quimica Inorganica-ICMA, The Universidad de Zaragaza-CSIC, Zaragaza-50009, Spain.
Haldia Institute Technolodgy, ICARE, Haldia, Midnapur, WB, India. E-mail: prithwis33@yahoo.com, pribatta@rediffmail.com.

Reaction of $[Au(C_6F_5)_2(OSO_2CF_3)_2]$ with RaaiR′ in dichloromethane medium followed ligand addition leads to $[Au(C_6F_5)_2(RaaiR')](OTf)$ [RaaiR′ = *p*-R-C_6H_4-N=N-C_3H_2-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), CH_2CH_3 (2), CH_2Ph (3), OSO_2CF_3 is the triflate anion, C_6F_5 is the pentafluorophenyl ring]. Ir spectra of the complexes show --C=N-- and --N=N-- stretching near at 1590 and 1370 cm^{-1} and near at 1510, 955, 800 cm^{-1} due to the presence of pentafluropheny ring. The ^1H NMR spectral measurements suggest methylene, –CH_2–, in RaaiEt gives a complex AB type multiplet while in $RaaiCH_2Ph$ it shows AB type quartets. In the ^1H-^1H COSY spectrum of the present complexes and contour peaks in the ^1H-^{13}C HMQC spectrum, assign the solution structure and stereoretentive transformation in each step.

Key words: Gold (III), arylazoimidazole, H, C, COSY, HMQC, electrochemistry, ESI mass.

INTRODUCTION

Transition metal complexes of diimine and related ligands have attracted much attention (Wilkinson et al., 1987; Schmidbaur, 1999; Dryden et al., 1992; Pramanik et al., 1997; Byabartta, 2005; Jemmis et al., 2000; Chattopadhyay et al., 2001). 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 (Schmidbaur, 1999; Byabartta, 2005; Uson et al., 1989), energy conversion and ability to serve as building blocks in supramolecular arrays (Greenwood and Earnshaw, 1989; Chakravarty and Chakravorty, 1983; Murray et al., 1995; Cerrada et al., 1995; Uson et al., 1989). Researchers have engaged in modifying the properties of Au-pyridine complexes by replacing the ligands of other donor centres, altering the steric and electronic properties of the ligands, differently substituted polypyridine mixed donor heterocycles. Gold (I) complexes, often containing phosphine and/or thiolato ligands, exhibit interesting photophysical and photochemical properties. Luminescence properties of gold (I) complexes, in particular, have been observed and experimentally studied for some years, owing, among others, to the wide range of wavelengths covered. Several publications,

including reviews, have addressed them. The nature of luminescence has been elusive to grasp. It is thought that the aurophilic interaction, the special closed shell attracttion between two filled d^{10} Au (I) centers, plays a role. Indeed, a large number of Au(I) luminescent complexes contain the Au(I) structural motif, and monomeric species may aggregate in solution or in the solid state, so that the origin of emission is assigned to a ligand to metal–metal bond charge transfer (LMMCT) transition and. On the other hand, not only transitions involving the Au–Au bonding orbital, but also metal to ligand charge transfer (MLCT) and ligand to metal charge transfer (LMCT) have been invoked as responsible for the luminescent behaviour of the complexes. The search for a suitable precursor to synthesize azoimine- complexes is a challenging domain and the compounds are found to be useful in this context [6]. A small number of scattered observations in the early structural chemistry of gold (I) complexes (Wilkinson et al., 1987; Schmidbaur, 1999; Dryden et al., 1992; Pramanik et al., 1997; Byabartta, 2005) 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 (Jemmis et al., 2000). In the present report new and note-worthy examples taken from the important class of gold pentafluorophenyl-azoimine. These compounds have interesting photophysical properties (Schmidbaur, 1999) and are relevant to homogeneous gold catalysis (Wilkinson et al., 1987) and to gold/silver thin film technology (Dryden et al., 1992). Prof. A Chakravorty has unfolded this ligands rhenium chemistry. But the gold chemistry and their organometallic chemistry with multinuclear NMR spectroscopy of this ligand system is totally unexplored. In this paper, we examine the reaction of RaaiR' on gold (III) pentafluorophenyl derivatives and the products are isolated. The complexes are well charecterised by ir, H nmr, C nmr, H-H COSY nmr, H-C HMQC and mass spectrometry.

EXPERIMENTAL

Published methods were used to prepare RaaiR' [7-9], [Au $(C_6F_5)_2(Br)_2$] NBu4. Microanalytical data (C, H and 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 nmr spectrometer using SiMe$_4$ as internal reference, CFCl$_3$ (external ^{19}F). Mass spectra were recorded on VG Autospec ESI usuing 3-nitrobenzyl as matrix.

Preparation of the complexes [bis(pentafluoropheny){1-ethyl-2-(p-tolylazo)imidazole}aurate(III)] triflate,Au($C_6F_5)_2$ (MeaaiEt)](OTf)$_2$, 2b.

To an dichloromethane slight yellow colour solution (15 cm^3) of [Au($C_6F_5)_2Br_2$] (0.945 g, 0.20 mmol) AgOTf was added (1:2) to produce de-bromo product, that is, Au($C_6F_5)_2(OSO_2CF_3)_2$ (0.20 mmol) into this, was added yellow dichloromethane solution of 1-ethyl-2-(p-tolylazo)imidazole, 0.039 g (0.20 < mmol) slowly, drop-wise, and the mixture was stirred at 343 - 353 K for 12 h. The red 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. Analytically pure complexes were obtained after chromatography over an alumina (neutral) column on eluting the red band with toluene-acetonitrile (4:1, v/v) and evaporating slowly in air. The yield was 0.088 g (80%). All other complexes were prepared similarly as stated above. Analysis for $C_{23}H_{10}N_4F_{13}AuOSO_2$, 1a, Calc(found): C, 32.34(32.38), H, 1.16(1.14), N, 6.56(6.57); IR ν(N=N) 1370, ν(C=N), 1590, ν(C_6F_5) 1510, 955, 800 cm^{-1} ESI mass, , 854.3 [M$^+$], 704.8 [M-OTf]; ^{1}H NMR, ppm, H(7,11), 8.07(d, J = 8Hz), H(8,10), 8.01(d, J=6.5Hz), H(9), 7.99(s,), H(4), 7.26(d, J=6Hz), H(5), 7.34(d, J=5Hz), CH$_3$ of Me, 1.5(t, J=6Hz); ^{19}F{H}NMR, ppm of (C_6F_5), -78.02(OTf), -120.03(F$_o$), -158.03(F$_p$), -159.12(F$_m$). ^{13}C{H}NMR, ppm, 134.2, 134.5,134.6, 134.7,134.9 (12C), 134.5(C2), 124(C4), 125(C5), 125.3(C7,11), 129.2(C8,10), 134(C6), 42,50(Me Gr.); Analysis for $C_{24}H_{12}N_4 F_{13}AuOSO_2$, 1b, Calc(found): C, 33.18(33.8), H, 1.34(1.4), N, 6. 6(6.37); IR ν(N=N) 1370 ν(C=N) 1590 ν(C_6F_5) 1518, 955, 800 cm^{-1} ESI mass, , 870.3 [M$^+$], 720.8 [M-OTf]; ^{1}H NMR, ppm, H(7,11), 8.02 (d, J = 8Hz), H(8,10), 8.09(d, J=6.5Hz), H(9-Me), 1.99, H(4), 7.21(d, J=6Hz), H(5), 7.34(d, J=5Hz), CH$_3$ of Me, 1.5(t, J=7Hz); ^{19}F{H}NMR, ppm of (C_6F_5), -78.02(OTf), -121.63(F$_o$), -158.83(F$_p$), -159.92(F$_m$). ^{13}C{H}NMR, ppm, 134.2,

134.5, 134.6,134.7,134.9 (12C), 134.6(C2), 124(C4), 124(C5), 124.3(C7,11), 128.2(C8,10), 134(C6), 40,50(Me Gr.); Analysis for $C_{24}H_{11}N_4 F_{13}AuClOSO_2$, 2c, Calc(found): C, 31.65(31.84), H, 1.26 (1.24), N, 6.16(6.17); IR ν(N=N) 1370 ν(C=N) 1590, ν(C_6F_5) 1510, 955, 800 cm^{-1} ESI mass, 904.3 [M$^+$], 754.8 [M-OTf]; ^{1}H NMR, ppm, H(7,11), 8.27(d, J = 8Hz), H(8,10), 8.21(d, J=6.5Hz), H(4), 7.26(d, J=6Hz), H(5), 7.34(d, J=5Hz), CH$_2$ of Et, 4.57(quartet, J=5.9,6.1Hz), CH$_3$ of Et, 1.5(t, J=6Hz); ^{19}F{H}NMR, ppm of (C_6F_5), -78.02(OTf), -121.03(F$_o$), -158.03(F$_p$), -159.12(F$_m$). ^{13}C{H}NMR, ppm , 134.2, 134.5,134.6,134.7,134.9 (12C), 134.5(C2), 124(C4), 125(C5), 125.3(C7,11), 129.2(C8,10), 134(C6), 42,50(Et Gr.); Analysis for $C_{23}H_9N_4F_{13}AuClOSO_2$, 1c, Calc(found): C, 31.04 (31.08), H, 1.06 (1.04), N, 6.396(6.39); IR ν(N=N) 1374 ν(C=N) 1599 ν(C_6F_5) 1510, 955, 800 cm^{-1} ESI mass, 888.5 [M$^+$], 738.8[M-OTf]; ^{1}H NMR, ppm, H(7,11), 8.27(d, J = 8Hz), H(8,10), 8.01(d, J=7.5Hz), H(9-H), 7.99(dd, J=7.86Hz), H(4), 7.26(d, J=6Hz), H(5), 7.34(d, J=5Hz), CH$_3$ of Me, 1.56(t, J=6Hz); ^{19}F{H}NMR, ppm of (C_6F_5), -78.02(OTf), -121.03(F$_{ortho}$), -158.03(F$_{para}$), -159.12(F$_{meta}$). ^{13}C{H}NMR, ppm , 134.2,134.5,134.6,134.7,134.9 (6C), 134.5(C2), 124(C4), 125(C5), 125.3(C7,11), 129.2(C8,10), 134(C6), 39,50(Me Gr.); Analysis for $C_{24}H_{12}N_4 F_{13}AuOSO_2$, 2a, Calc(found): C, 33.18(33.8), H, 1.34(1.4), N, 6. 6(6.37); IR ν(N=N) 1370 ν(C=N) 1590 ν(C_6F_5) 1518, 955, 800 cm^{-1} ESI mass, 870.3 [M$^+$], 720.8 [M-OTf]; ^{1}H NMR, ppm, H(7,11), 8.02 (d, J = 8Hz), H(8,10), 8.09(d, J=6.5Hz), H(9-Me), 1.99, H(4), 7.21(d, J=6Hz), H(5), 7.34(d, J=5Hz), CH$_3$ of Me, 1.5(t, J=7Hz); ^{19}F{H}NMR, ppm of (C_6F_5), -78.02(OTf), -121.63(F$_o$), -158.83(F$_p$), -159.92(F$_m$). ^{13}C{H}NMR, ppm, 134.2,134.5,134.6, 134.7,134.9(12C), 134.6(C2), 124(C4), 124(C5), 124.3(C7,11), 128.2(C8,10), 134(C6), 40,50(Me Gr.); Analysis for $C_{25} H_{15} N_4$ $F_{13}AuOSO_2$, 2b, Calc(found): C, 33.94(33.8), H, 1.71(1.64), N, 6.33(6.97); IR ν(N=N) 1370 ν(C=N) 1595 ν(C_6F_5) 1510, 955, 800 cm^{-1} ESI mass, 884.3 [M$^+$], 734.8 [M-OTf]; ^{1}H NMR, ppm, H(7,11), 8.27(d, J = 8Hz), H(8,10), 8.21(d, J=6.5Hz), H(4), 7.26(d, J=6Hz), H(5), 7.34(d, J=5Hz), CH$_2$ of Et, 4.57(quartet, J=5.9,6.1Hz), CH$_3$ of Et, 1.5(t, J=6Hz); ^{19}F{H}NMR, ppm of (C_6F_5), -78.02(OTf), -118.93(F$_o$), -156.43(F$_p$), -159.10(F$_m$). ^{13}C{H}NMR, ppm, 134.2, 134.5,134.6, 134.7,134.9 (12C), 129.1, 129.3-130.4, 134.5(C2), 124(C4), 125(C5), 125.3(C7,11), 129.2(C8,10), 134(C6), 42,50(Et Gr.); Analysis for $C_{29} H_{13} N_4$ $F_{13}AuOSO_2$, 3a, Calc(found): C, 37. 4(37.8), H, 1.36(1.34), N, 6.06(6.07); IR ν(N=N) 1376 ν(C=N) 1590 ν(C_6F_5) 1510, 955, 800 cm^{-1} ESI mass, M, 930.3 [M$^+$], 780.8 [M-OTf]; ^{1}H NMR, ppm, H(7,11), 8.27(d, J = 8Hz), H(8,10), 8.21(d, J=7.5Hz), H(CH$_3$), 1.99(s,), H(4), 7.26(d, J=6Hz), H(5), 7.34(d, J=5Hz), CH$_2$ of Bz, 4.57(quartet, J=5.9,6.1Hz), Ph of Bz, 7.5-7.6; ^{19}F{H}NMR, ppm of (C_6F_5), -78.02(OTf), -121.93(F$_{or}$), -158.93(F$_p$), -159.92(F$_m$). ^{13}C{H}NMR, ppm, 134.2,134.5, 134.6,134.7,134.9 (6C), 129.1,129.3-130.4, 134.5(C2), 124(C4), 125(C5), 125.3(C7,11), 129.2(C8,10), 134(C6), 129-130, 42,50(Bz Gr.); Analysis for $C_{30} H_{15}$ N_4 $F_{13}AuOSO_2$, 3b, Calc(found): C, 38.14(38.18), H, 1.6(1.4), N, 5.96(5.87); IR ν(N=N) 1370 ν(C=N) 1590 ν(C_6F_5) 1510, 955, 800 cm^{-1} ESI mass, 944.3 [M$^+$], 794 [M-OTf]; ^{1}H NMR, ppm, H(7,11), 8.27(d, J = 8Hz), H(8,10), 8.21(d, J=6.5Hz), H(9-CH$_3$), 1.99(s,), H(4), 7.26(d, J=6Hz), H(5), 7.34(d, J=5Hz), CH$_2$ of Bz, 4.96(quartet, J=5.9,6.1Hz), Ph of Bz, 7.5-7.9; ^{19}F{H} NMR, ppm of (C_6F_5), -78.02(OTf), -121.03(F$_o$), -158.03(F$_p$), -159.12(F$_m$). ^{13}C{H} NMR, ppm, 134.2,134.5,134.6,134.7,134.9 (12C), 134.5(C2), 124(C4), 125(C5), 125.3(C7,11), 129.2(C8,10), 134(C6), 129-130, 42,50(Bz Gr.); Analysis for $C_{29} H_{12} N_4$ $F_{13}AuClOSO_2$, 3c, Calc(found): C, 36.04(36.8), H, 1.26(1.24), N, 5.6(4.7); IR ν(N=N) 1377 ν(C=N) 1590 ν(C_6F_5) 1510, 955, 800 cm^{-1} ESI mass, 964.3 [M$^+$], 814.8 [M-OTf]; ^{1}H NMR, ppm, H(7,11), 8.27(d, J = 8Hz), H(8,10), 8.21(d, J=6.5Hz), H(CH$_3$), 1.99(s,), H(4), 7.26(d, J=6Hz), H(5), 7.34(d, J=5Hz), CH$_2$ of Bz, 5.057(quartet, J=5.9,6.1Hz), Ph of Bz, 7.5-7.9; ^{19}F{H} NMR, ppm of (C_6F_5), -78.02(OTf), -121.93(F$_o$), -158.93(F$_p$), -159.12(F$_m$). ^{13}C {H} NMR, ppm, 134.2, 134.5, 134.6, 134.7, 134.9

$$[Au(C_6F_5)_2Br_2]NBu_4 \quad + 2\ AgOTf \longrightarrow \quad [Au(C_6F_5)_2(OTf)_2]NBu_4 + 2\ AgBr$$

RaaiR

$$[Au(C_6F_5)_2(RaaiR)](OTf) + NBu_4OTf$$

R = H(a), Me(b), Cl(c)
R´= Me(1), Et(2), Bz(3)

Scheme 1.

Isomer A   Isomer B
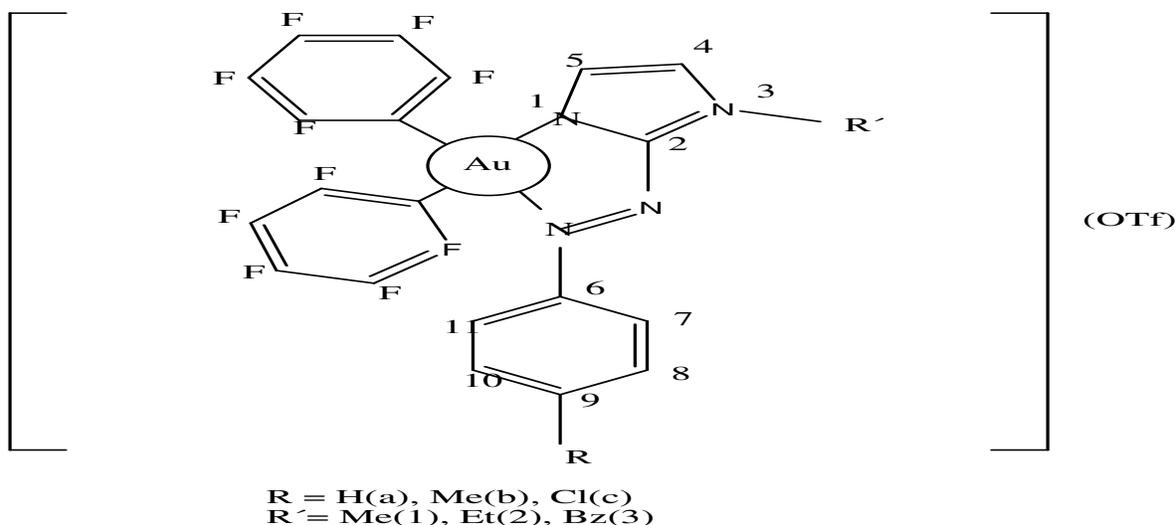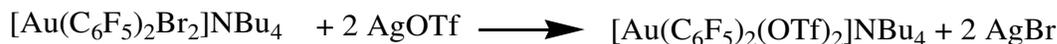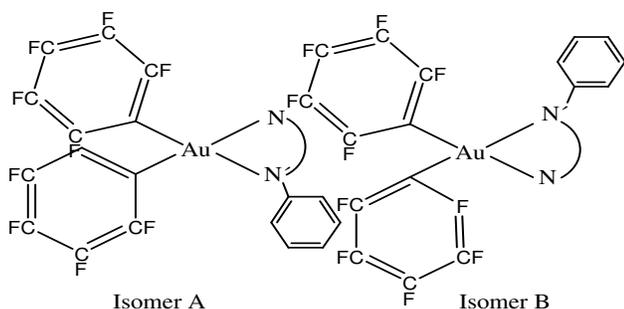
Scheme 2.

(6C), 134.5(C2), 124(C4), 125(C5), 125.3(C7, 11), 129.2(C8, 10), 134(C6), 129 -130, 42, 50(Bz Gr.).

RESULTS AND DISCUSSION

The complexes [Au (C$_6$F$_5$)$_2$(RaaiR$^{/}$)] (OTf), were prepared by removing weakly coordinating triflate ion, OSO$_2$CF$_3$, from [Au (C$_6$F$_5$)$_2$(OSO$_2$CF$_3$)$_2$], with RaaiR$^{'}$ under stirring at 343 - 353 K in dichloromethane solution in good yield (75 - 80%). The synthetic routes are shown in Scheme 1. The composition of the complexes is supported by microa-

nalytical results. The red orange complexes are soluble in common organic solvents viz. acetone, acetonitrile, chloroform, dichloromethane but insoluble in H$_2$O, methanol, ethanol. In MeCN, the complexes, (1 - 3) behave as 1:1 electrolytes (Λ_M = 40 - 60 Ω^{-1}cm^{-1}mol^{-1}). Ammonium tetrabutyl triflate is very much interfering although the complexes are well washed with hexane and ether to remove this, but it stays in a slight amount, so the NMR signals become complicated with the butyl peaks that are not expected. The ESI mass spectrum of a MeCN solution in the positive ion mode is structurally enlightening, since it displays a series of characteristic singly. The maximum molecular peak of (3c) is observed at m/z 964.5 (12%), which corresponds to the molecular ion, where calculated molecular weight is 964.03. A very careful examination of the fragmentation pattern of the ESI mass spectrum reveals the stepwise elimination of triflate ion (m/z at 814.51, 40%). Ir spectra of the complexes, [Au(C$_6$F$_5$)$_2$(Ra aiR$^{/}$)] show a 1:1 correspondence to the spectra of the tetrahydrothiophene analogue, except the appearance of intense stretching at 1365-1370 and 1570 - 1580 cm^{-1} with concomitant loss of ν(Au-Br) at 320 - 340 cm^{-1}. They are assigned to ν(N=N) and ν(C = N) appear at 1365 - 1380 and 1570 - 1600 cm^{-1}, respectively. Other important frequencies are ν(C$_6$F$_5$) at 1510 - 1520, 950 - 960 and

Figure 1. Carbon NMR of complex 1b and 2c, Fluorine NMR of complex 1c.

790 - 810 cm^{-1} along with weak bands at 1070 and 1072 cm^{-1}. The ^{1}H nmr spectra of [Au (C$_6$F$_5$)$_2$(RaaiR$^{/}$)] (OTf) (1-3) complexes were unambiguously assigned (measured in CDCl$_3$) on comparing with [Au (C$_6$F$_5$)$_2$(Br)$_2$] NBu4 and the free ligand (RaaiR$^{/}$) (Byabartta, 2005; Jemmis et al., 2000; Greenwood and Earnshaw, 1989). Imidazole 4- and 5-H appears as doublet at the lower frequency side of the spectra. The aryl protons 7-(7$^{/}$-) and 11-(11$^{/}$-) H resonate asymmetrically indicative of a magnetically anisotropic environment (Byabartta, 2005) even in the solution phase. The aryl protons (7-H - 11-H) of are downfield shifted by 0.1-0.7 ppm as compared to those of the parent derivatives (Byabartta, 2005; Jemmis et al., 2000). 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 1-R$^{/}$ [R$^{/}$ = Me, CH$_2$CH$_3$, CH$_2$ (Ph)] exhibit usual spin-spin interaction. 1-Me appears as a singlet at 4.2 ppm for Au(C$_6$F$_5$)$_2$(RaaiMe); the methylene protons, 1-CH$_2$-(CH$_3$) show AB type sextet and (1-CH$_2$)CH$_3$ gives a triplet at 1.5 ppm for [Au(C$_6$F$_5$)$_2$(RaaiCH$_2$CH$_3$)]. 1-CH$_2$ (Ph) protons appear at AB type quartets in [Au (C$_6$F$_5$)$_2$(RaaiCH$_2$Ph)]. The aryl-Me (R = Me) in [Au (C$_6$F$_5$)$_2$(MeaaiR$^{/}$)] appears as a single signal at 2.30 ppm. Fluorine n.m.r., ^{19}F {H}, is very much important of the present series of complexes (measured in CDCl$_3$). Among five fluorine atoms in each complexes, they show three sharp signals which are corresponds to two ortho, two meta and one para fluorine atom, respectively, of the pentafluorophenyl ring of the complexes with the addition of a peak for the triflate ion (Figure 1). The ^{13}C nmr spectrum provides direct information about the carbon skeleton of the molecule (Figure 1). Carbon atoms neighbouring the nitrogen atom shifted to downfield due to an increased electron density resulting from the presence of electronegative nitrigen atom and pi electron delocalisation in the magnetic environment. The carbon atom adjacent to the pentafluorophenyl ring 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 40 ppm, resonably compare to the other carbon atoms resonance. The COSY spectrum reveals the ^{1}H-^{1}H coupling interactions in the molecule. The comperatively weaker coupling interections of C(8)H and C(10)H with the far apart positioned C(4)H and C(5)H protons of the imidazole moity are shown by the poorly resolved cross peaks at δ = 7.32 ppm and 7.33 ppm. The ^{1}H-^{13}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. The electrochemical properties of the com-plexes were examined cyclic voltammetrically at a glassy carbon working electrode in MeCN and the potentials are referred to SCE. The voltammogram not display gold oxidation couple at positive side but show the ligand reductions at the negative to SCE. 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 -0.90 to -1.04. 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, ΔE$_p$>110 mV. Two redox couples at negative to SCE are due to reductions of ligand (second one at -1.0 to -1.2). Arylazoimidazoles can accommodate two electrons at LUMO mostly characterised by azo group. These two couples may be due to azo$^-$/azo redox reaction of coordinated RaaiR$^{/}$ ligand.

In conclusion, this work describes the isolation of a novel series of Gold (III) azo-imine complexes with an organometallic link with pentafluorophenyl ring, [Au (C$_6$F$_5$)$_2$(RaaiR$^{/}$)] (OTf) and their spectral and elemental characterisation. ^{1}H NMR study suggests quartet splitting of ethyl substitution. ^{19}F {H} NMR show three sharp signals which is lower than the parent complex. ^{1}H-^{1}H COSY spectrum and ^{1}H-^{13}C HMQC spectrum assign them to the carbon hydrogen atoms interection and contour respectively. Electrochemistry gives further information on ligand reduction. ^{13}C (^{1}H) NMR tells the molecular skeleton.

REFERENCES

Byabartta P (2005). Synthesis, spectral characterisation and redox properties of heteroleptic ruthenium(II)–p-tolylazoimidazole–pyridine complexes. Transition Met. Chem. 30-575.

Byabartta P (2005). Synthesis, spectral studies, crystal structure and redox properties of homoleptic tris-chelated ruthenium(II) – arylazoimidazoles. Transition Met. Chem. 30-902.

Byabartta P (2005). The synthesis, spectral and electrochemistry of 8-Quinolinato)-bis- {1-alkyl-2-(arylazo) imidazole} Ruthenium (II) hexafluorophosphate: Single crystal X-ray structure of [Ru(Q)(MeaaiMe)2](PF6).CH2Cl2 [Q = 8-quinolinolate, MeaaiMe = 1-Methyl-2-(p-tolylazoimidazole)]. Transition Met. Chem. 30-672.

Byabartta P (2005). A novel series of sulphur-bridged ruthenium-molybdenum complexes: [(RaaiR¢)2 Ru(l-S)2Mo(OH)2]. Synthesis, spectroscopic and electrochemical characterization. RaaiR¢=1-alkyl-2-(arylazo) imidazole. Transition Met. Chem. 30-672.

Cerrada E, Fernandez EJ, Gimeno MC, Laguna A, Laguna M, Termba R, Villacampa MD (1995). A novel series of golden complexes: Synthesis, spectroscopic and electrochemical characterization. J. Organomet. Chem. 492 -105.

Chakravarty AR, Chakravorty A (1983). Synthesis, spectra and electrochemistry of dinitro-bis-{1-alkyl-2-(arylazo) imidazole}ruthenium(II). Nitro-nitroso derivatives and reactivity of the electrophilic {Ru-NO}6. J. Chem. Soc. Dalton Trans. 961.

Chattopadhyay S, Ghosh K, Pattanayak S, Chakravorty A (2001). Ruthenium-azoimine-chloranilates synthesis, spectra and electrochemistry of ruthenium(II)-1-alkyl-2-(arylazo)imidazole-chloranilate complexes. J. Chem. Soc. Dalton Trans. 1259.

Dryden NH, Shapter JG, Coatesworth LL, Norton PR, Puddephatt R (1992). chloranilates synthesis, spectra and electrochemistry of ruthenium(II)-1-alkyl-2-(arylazo)imidazole- complexes. J. Chem. Mater. 4 – 979.

Greenwood NN, Earnshaw A (1989). Chemistry of the Elements, Pergamon Press, Oxford p. 519.

Jemmis ED, Subramanian G, Nowek A, Gora RW, Sullivan RH, Leszczynski J (2000). A novel series of gold(III)-bis-triphenylphosphine-arylazoimidazole complexes: synthesis and spectroscopic and redox study. J. Mol. Struct. 556-315.

Murray HH, lwen Wl, Sherman SE, Greaney MA, Edksen KA, Carstense BA, Halhbert TR, Sliefel EI (1995). Synthesis, spectral characterization, redox studies of isomeric dichlorobis-[1-alkyl-2-(naphthyl-(α/β)-azo)imidazole]ruthenium(II). Single crystal X-ray structure of blue-green dichloro-bis-[1-ethyl-2-(naphthyl-α-azo) imidazole]ruthenium(II). Angrew. Chem. 34-841.

Pramanik K, Ghosh P, Chakravorty A (1997). Synthesis, spectroscopic and electrochemical studies of isomeric dichloro bis- [N(1)-alkyl-2-(arylazo)imidazole] osmium(II). Single crystal X-ray structures of blue-violet dichloro-bis-[N(1)-methyl-2-(arylazo)imidazole] osmium(II) species. J. Chem. Soc. Dalton Trans. 3553.

Schmidbaur HG (1999). Progress in Chemistry, Biochemistry and Technology, John Wiley and Sons Chichester. Nitro-ruthenium(II)-arylazoimidazoles: Synthesis, spectra, crystal structure and electrochemistry of dinitro-bis-{1-alkyl-2-(arylazo)imidazole} ruthe-nium(II). Nitro-nitroso derivatives and reactivity of electrophilic {Ru-NO}[6] system.

Uson R, Laguna A, Laguna M (1989). Synthesis, spectral characterization and electrochemical properties of osmium (II) complexes of 1-ethyl-2-(arylazo)imidazoles. Inorg. Synth. 26- 85.

Wilkinson G, Gillard RD, McCleverty JA (1987). Editors, Comprehensive Coordination Chemistry vol. 2, Pergamon, Oxford (Chapter 55 and references therein).